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Physics. — "*Solid helium*" [1]). By W. H. KEESOM. (Communication N⁰. 184*b* from the Physical Laboratory at Leyden).

(Communicated at the meeting of September 25, 1926).

§ 1. *Introduction.*

On the same day that KAMERLINGH ONNES liquefied helium for the first time, he investigated whether it would become solid on further cooling by evaporation under reduced pressure. He was at that time able to obtain a vapour pressure below 1 cm, probably 7 mm [2]). The helium however remained liquid.

This attempt to solidify helium by reducing the pressure under which it evaporates, was repeated on several occasions. In 1909 KAMERLINGH ONNES was able to reduce the pressure to 2.2 mm (the temperature then was estimated at 2.5 to 2° K., now put at 1.4° K.) [3]); in 1910 a pressure of even 0.2 mm was reached (temperature 1.15° K.) [4]). But the helium still remained a thin liquid.

The further development of the question, whether helium could be made to freeze on still further cooling, was then postponed in favour of more urgent questions, which could be dealt with the means available, while for the investigation of the solidification of helium new means were necessary. [5]).

A new attempt was made in 1919, but with little improvement. Then in 1921 KAMERLINGH ONNES [6]) by making use of a battery of condensation pumps, reached a remarkably lower pressure, probably 0.013 mm, at any rate less than 1/50 mm, at which, after estimation, the temperature should be 0.82° K.

Meanwhile helium still remained liquid, so that KAMERLINGH ONNES wondered whether helium would perhaps remain liquid even if it were cooled to the absolute zero. In order to obtain further data about this question KAMERLINGH ONNES still before his retirement procured a much more powerful mechanical pump installation, and further, a condensation pump of greater power was constructed with which we intend to reduce the temperature again.

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[1]) Provisional communications were published in C. R. **183**, 26 and 189, July 5 and 19, 1926, and Nature July 17, 1926.

[2]) These Proc. **11**, 168, 1908; Comm. Leyden, N⁰. 108.

[3]) These Proc. **12**, 175, 1909; Comm. Leyden, N⁰. 112.

[4]) Jubilee-Book VAN BEMMELEN 1910. See also Comm. Leyden N⁰. 119, p. 12 and Comm. Leyden Suppl. N⁰. 35, p. 29.

[5]) See KAMERLINGH ONNES, Comm. Leyden N⁰. 159, § 4.

[6]) H. KAMERLINGH ONNES, Comm. Leyden N⁰. 159.

Meanwhile the results of the provisional experiments of KAMERLINGH ONNES and VAN GULIK [1]) about the change of the melting point of hydrogen by pressure, had made me wonder, if it would not be possible at the temperatures already reached, to solidify helium by pressure. This idea became still more definite on considering the results of the measurements of SIZOO and KAMERLINGH ONNES [2]) about the influence of allsided compression on the supraconductivity: so fig. 5 of Comm. N⁰. 180*b* raised the question, whether the small difference between the lines for 193 and for 300 KG/cm² (according to the authors hardly more than experimental error), would not be explained thus: that the helium had become solid in the compression tube and that because of the adhesion to the wall an increase of the pressure put on had not caused a corresponding increase of the pressure upon the investigated thread [3]).

§ 2. *Solidification of helium* (June 25th 1926). *Provisional determination of the melting curve.*

a. *Method.* The criterion for judging if helium had become solid, and

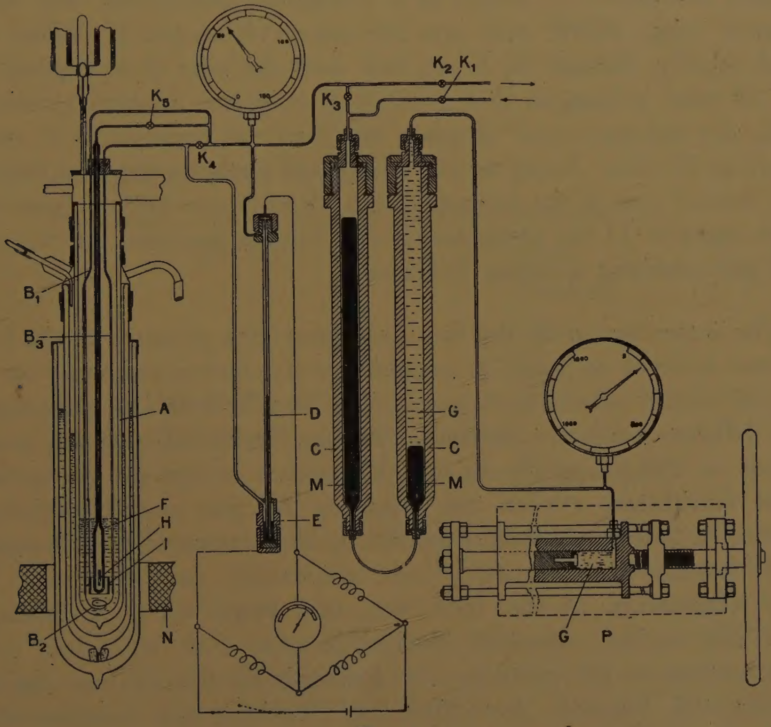

Fig. 1.

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[1]) H. KAMERLINGH ONNES and W. VAN GULIK, These Proc. 29, p. 1184, 1926; Comm. Leyden N⁰. 184*a*.

[2]) These Proc. 28, 656, 1925; Comm. Leyden N⁰. 180*b*.

[3]) See also G. J. SIZOO, W. J. DE HAAS and H. KAMERLINGH ONNES, Comm. Leyden N⁰. 180*c*, p. 32 and fig. 2.

the method for determining the melting curve of the solid helium were the same as those followed by KAMERLINGH ONNES and VAN GULIK (l.c.) in determining the melting curve of hydrogen.

In fig. 1, B_1 and B_3 are two tubes of new silver, which are connected at the bottom, in the cryostat vessel A, by a narrower brass tube B_2. Here the helium is compressed. Therefore firstly the wheel of the hydraulic pump P, which is filled with glycerine G, is turned back. CC are two vessels, connected by a tube, which are half-filled with mercury M. By turning back the wheel, glycerine comes into the pump, the mercury rises in the right hand vessel C, and falls in the left hand one. So the left hand vessel gets filled with helium gas, which is supplied by the stop-cock K_1 (K_3 is shut). Then K_1 is shut, K_3 opened. K_4 is open, K_2 shut [1]). Now by turning the wheel of the hydraulic pump to the right the helium gas is compressed into the tubes B, in which it liquefies, and collects in the lower part of the tube. At a pressure of 400 KG/cm^2 all connections were still tight.

In order to determine if helium had solidified, the following apparatus was used, constructed by G. J. FLIM, chief of the technical staff of the cryogenic laboratory. D works as a differential manometer, and consists of a steel tube, which runs into the mercury-chamber E. When K_2 is opened slightly, K_4 and K_3 being shut, and the tube B is blocked by a piece of solid helium, so that a pressure difference appears between B_1 and B_3, the pressure in D becomes less than the pressure in E, and the mercury in D rises. Along the axis of D a thin platinum wire was stretched, which formed one of the branches of a Wheatstone bridge. Now when mercury rises in D the resistance of this branch decreases, and the needle of the galvanometer becomes deflected.

b. The experiments. In the first experiment the pressure of the helium bath was lowered as much as possible by the means ordinarily at hand in the laboratory (Burckhardtpump, 360 m^3/hour), namely to approximately half a millimeter mercury pressure. Within the capillary B the pressure was put at 250 KG/cm^2 [2]). In the Wheatstone bridge the galvanometer was at equilibrium. When the stopcock K_2 was opened slightly, the galvanometer needle showed a deflection. This indicated that the capillary B was blocked.

The temperature of the bath was now raised till the pressure was 1 atm. The capillary remained blocked.

The pressure in the capillary was lowered. At 150 KG/cm^2 the capillary was still blocked. At 100KG/cm^2 blocking had disappeared. At

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[1]) In the experiments of June 25th the side-tube with stopcock K_5 and the glass piezometer F were not present, in the experiments of July 1st K_5 was shut during the operation described above.

[2]) Here are given the apparent readings of the metalmanometer. In table I the corrections are applied.

130 KG/cm^2 the capillary was blocked again, as also at 128. At 125 KG/cm^2 it was open, and at 126 KG/cm^2 also.

Inference: at 126 KG/cm^2 helium is liquid, at 128 KG/cm^2 it is solid.

As in this experiment there was no stirrer in the cryostat, the temperature of the bath under the liquid surface was uncertain 1)).

The pressure of the helium bath was then reduced to about 2)) 400 mm. At 120 KG/cm^2 the capillary was blocked; so it was at 115.

At 110 KG/cm^2 capillary opens.
„ 112 „ „ blocked.
„ 111 „ „ still blocked.
„ 110 „ „ opens.

This result clearly showed that we were on the track of the melting curve of helium.

The pressure of the helium bath was reduced to about 200 mm.

At 95, 92, 90, 88 KG/cm^2 capillary is blocked.
" 85 " " opens.
" 88 " " blocked.
" 86 " " opens.

Reduced to about 100 mm.

At 80, 74, 69, 67 KG/cm^2 capillary blocked.
" 63, 65 " " open.
" 70 " " blocked.
" 65 " " open.

Reduced to about 50 mm.

At 55, 52 KG/cm^2 capillary blocked.
" 50 " blocking disappears gradually.

The bath was then brought to atmospheric pressure, but the observations were irregular; apparently the temperature of the bath was not uniform.

The bath was then reduced to about 400 mm. At 110 KG/cm^2 the blocking was gradually disappearing. On repetition the same was observed at 109 KG/cm^2. Thus the same result was obtained as in the first experiment at this temperature (see above). The phenomenon is reproducible.

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1) Indeed it appears from the results, obtained in the repetition of the experiment on July 1st, that the temperature in the lower parts of the bath was below the boiling point of helium.

2) Exact measurements were not made in this first series of experiments.

The provisional results, obtained on this day, are collected in the following table:

TABLE I.

Pressure of the helium bath	Temperature 1)	Melting pressure			Difference with determination of July 1st
		Manometer reading	Corrected 2) KG/cm^2	Atm.	
400 mm	3.61° K.	110	109^5	106	— 2
200	3.12	86	83	81	— 1
100	2.73	65	63^5	61^5	— 1^5
50	2.40	50	48	46	— 1

§ 3. *Repetition on July 1st. Determination of the melting curve. Visual observations.*

a. Determination of the melting curve of helium. Notwithstanding the distinctness of the phenomena I wished to make quite sure and to repeat the experiment. This was done on July 1st.

This time a stirrer (*I* in fig. 1, a hollow soft-iron cylinder, see under *b*, provided with a couple of little paddle-boards in order to stir the liquid) was introduced into the bath, and further arrangements were made, in order to be able to take more exact measurements 3). Further it was intended to continue the melting curve to the lowest temperatures, which could be reached with the mechanical vacuumpumps.

Moreover, now that it had appeared that the pressures ought not to be so excessively high, I wished to make the experiment in a glass piezometer, so as to be able to see what happened.

The determination of the melting curve occurred in exactly the same way as the provisional determinations mentioned in § 2*a*. The phenomena took place regularly. The melting pressure, corresponding to a definite temperature, could be fixed to some few tenths of an atmosphere. In some cases the fusion-process could be followed on the pointer of the galvanometer.

For the sake of brevity only the results obtained are given here.

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1) From the pressure of the bath calculated after the formula of Comm. Leyden N^0. 147*b*.

2) The metal manometer used (reaching to 400 KG/cm^2) was gauged to 100 KG/cm^2 with the aid of the closed hydrogen manometers M_{60} and M_{120}. Above this it was compared with the pressure balance of the VAN DER WAALS foundation at Amsterdam. I render therefore my cordial thanks to Dr. A. MICHELS, assistant of this foundation.

3) The pressure of the bath, from which the temperature was derived, was read off by Miss J. L. SOLLEWIJN GELPKE, phil. nat. cand.; for this aid I render to her my cordial thanks.

TABLE II.

Melting curve of helium		
Pressure of the helium bath	Temperature	Melting pressure
77.09 cm	4.21 °K.	140.5 atm.
40.03	3.61	108.8
20.01	3.12	81.5
9.94	2.72	62.8
5.02	2.40	48.6
2.00	2.04	35.7
1.10	1.83	29.8
0.57	1.60	27.4
0.24	1.42	26.5
0.057	1.19	25.3

The temperatures from 4.21 down to and including 1.60° K. are derived from the pressures of the helium bath according to the formula of Comm. N^0. 147*b* [1]), the two lowest temperatures from the formula which is given by VERSCHAFFELT in Comm. Leyden Suppl. N^0. 49, p. 26 [2]).

The melting pressures were read off on a metal manometer (reading to 150 KG/cm^2) which was gauged to 100 KG/cm^2 with the aid of a manometer, which was itself compared with the closed hydrogen manometers M_{60} and M_{120} [3]).

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[1]) H. KAMERLINGH ONNES and S. WEBER. These Proc. **18**, 493, 1915.

[2]) In the provisional communication in the C.R. for these lowest temperatures, values are also communicated which were calculated from a former formula of VERSCHAFFELT (Thesis for the Doctorate TUYN, Comm. Leyden N^0. 181). I prefer now the values only given here.

[3]) When the experiments mentioned in § 4 were finished, it was found that the pointer of this manometer was not securely fastened on its axis, and that the zero reading was changed.

As it is not sure if this occurred before or after the experiment of July 1st, these pressure measurements must not be considered absolutely sure. Also for the same reason the corrections above 100 KG/cm^2 could not be determined afterwards. They were derived from comparison of the manometer with the pressure balance of the VAN DER WAALS foundation, done in Sept., by adopting a constant zero change. This zero change is derived from the difference between this gauging with the pressure balance and the gauging with M_{60} and M_{120}, mentioned in the text, for pressures below 100 KG/cm^2. I give here the results which for the moment I think to be the most probable ones, reserving the right to repeat this measurement.

[Such a repetition took place at Nov. 26th, 1926. The pressures of table II were confirmed within some tenths of an atmosphere. At the average the readings were 0.6 atm. higher at Nov. 26th. Added in the translation.]

These measurements are sufficiently in agreement with those of § 2a (table I) to form a confirmation of the observations of June 25th.

In fig. 2 the melting curve is represented.

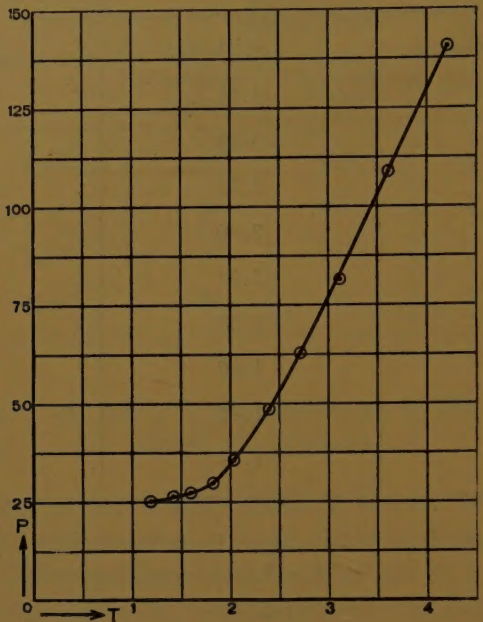

Fig. 2.

The melting curve shows an important peculiarity: it bends at the lowest temperatures so as to become more and more parallel to the *T*-axis. It shows no tendency at all to meet the vapour pressure curve in a triple-point [1]. So unless the melting curve bends down again to the *T*-axis at still lower temperatures, it will never be possible to solidify helium, liquid under its own saturation pressure, by lowering the temperature alone. So the surmise expressed by KAMERLINGH ONNES (see § 1) that helium (under its own saturation pressure) remains liquid down to the absolute zero (perhaps gradually changing into the vitreous amorphous state), would be established.

In the supposition mentioned, that the melting curve does not bend down again at lower temperatures so that the melting curve and the vapour pressure curve do not meet, as long as we remain below the liquid-gas critical temperature, coëxistence between solid and gas is not possible. Then there is no sublimation curve; evaporation of the solid into the gaseous state will not be possible at those temperatures, the solid will always melt first [1]). This is yet another peculiarity, which distinguishes helium from all other substances as far as we can judge from observations already made.

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[1] As Prof. KRUYT pointed out to me, the possibility that this might occur with some substance was already foreseen by H. W. BAKHUIS ROOZEBOOM, Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre, Braunschweig 1901, p. 93. (Note added in the translation).

The approaching to zero of dp/dT of the melting curve indicates according to the equation of CLAPEYRON, that the heat of fusion approaches in a higher power of T to zero than $T(v_{liq} - v_{sol})$. This is in agreement with the heat theorem of NERNST, when this is applied to the change liquid-solid helium, and perhaps forms, as EHRENFEST remarked, one of the most elementary confirmations of it.

b. Visual observations on the solidification of helium. For this purpose there was brought into the helium cryostat a glass piezometer F (inner diam. 7, outer diam. 13, length 90 mm), into which the helium was supplied by stopcock K_5. Inside this piezometer was a small soft-iron rod H, which functionned as an electromagnetic stirrer (method of KUENEN). It was moved up and down with the aid of the cylinder I, which was magnetized by the current passing through the windings of the coil N. The cylinder I served also for stirring the helium bath, in order to obtain a uniform temperature (see under *a*).

After the measurements, mentioned under *a*, were finished helium was compressed into the glass piezometer.

The pressure of the helium bath was 13.3 mm, to which corresponds a temperature of 1.90° K. While the pressure within the piezometer was increased [2]), the stirrer was constantly moved up and down. At a certain pressure the stirrer stuck; the helium had become solid. There was however nothing peculiar to be seen in the tube. Solid helium is perfectly transparent.

On decreasing the pressure the stirrer becomes free. Increase of pressure makes the stirrer stick again. These experiments were finished at $3^h.30$.

The experiment was repeated at $5^h.30$. The level of the helium bath was now somewhat higher (about $^2/_3$ of the piezometer was in the liquid [1])). The pressure of the helium bath was now 200 mm, corresponding to a temperature of 3.12° K.

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[1]) When the melting curve continues to temperatures above the liquid-gas critical temperature, of course for those temperatures there will be a direct evaporation of the solid into the gaseous state.

[2]) There now separated from the helium at the top of the tube a white flaky mass, which stayed for some time in this position, giving the impression of being of very loose structure. By the action of the stirrer H, small pieces occasionally got loose, and sank down in the liquid helium. They probably consisted of condensed oil vapours, which were present in the helium coming from the cycle in more than the usual (very small) quantity, because, during the preceding experiments the helium liquefactor was heated, and the oil vapours which had collected in it in the condensed state, were now scattered throughout the helium gas, particularly in that part of the cycle from which the gas to be compressed was sucked into the piezometer.

In the course of the experiment by the action of the stirrer this mass is spread over the inner wall as a nearly invisible deposit. On repetition of the experiment, in which the piezometer was filled, while the helium liquefactor was still cold, so that the oil vapours remained in the liquefactor, this phenomenon did not occur.

At 90 KG/cm^2 the stirrer is still loose, at 90.5 KG/cm^2 it sticks. On decreasing the pressure to 87 KG/cm^2 it becomes loose again. Evidently there is some delay in the phenomenon, as a result of the less rapid temperature adjustment owing to the thickness of the glass walls. Otherwise this observation is sufficiently in agreement with that of table II, for complete confirmation, that in these experiments we had observed helium solidifying.

Again there is nothing peculiar to be seen in the helium; no surface of demarcation between solid and liquid, nor between solid and gas or between liquid and gas [2]).

There was no indication of difference in refraction, nor change of volume. Evidently the densities and the refractive indices of the different phases under these pressures are nearly equal.

Helium solidifies to a homogeneous transparent mass. That it is a cristalline mass, seems to follow from the fact that the melting curve is sharply defined (comp. under *a*).

The following detail of the experiment is very instructive. At one moment the helium was liquid in the lowest part of the glass tube, where the stirrer was affixed; above it was a mass of solid helium. This appeared from the fact that the stirrer could be moved only to a definite height, where it collided against the solid block. We were able to hammer the solid helium. Very gradually the stirrer could be moved higher and higher; the block slowly melted down, probably in consequence of the temperature increasing slowly by the radiation of the lamp, which served for illumination.

Even now there was no limiting surface between solid and liquid to be seen.

§ 4. *Demonstration on July 7th.*

I had the pleasure on the occasion of the American week to demonstrate the solid helium to the American students who payed a visit to the laboratory and to some colleagues and others who were interested in it. The experiment of hammering against the block could now be repeated several times. When helium has solidified by increasing the pressure just a little above the melting pressure, and we then decrease the pressure a little, sufficiently to melt the helium slowly, the melting occurs firstly round the stirrer, the stirrer absorbing the radiation of the illumination lamp more than the transparent helium and so acquiring a slightly higher temperature than the helium. So the stirrer gets loose before the helium melts "en masse".

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[1]) In the preceding experiment $^1/_4$, about the length of the stirrer, 23 mm.

[2]) As regards the last it should be noted, that immediately above the level of the helium in the bath there is a large temperature gradient, so there must be a rapid transition from either the liquid or the solid phase to the gaseous one.

The following observation is very well worth mentioning.

Towards the end of the demonstration, the helium being compressed in the tube more than ten times, there were in the compressed helium some very small dark particles, apparently oxide from the metal tube, which connects the glass experimenting tube with the other apparatus. Then on one occasion I noticed that, resulting from a blow of the stirrer, a mass of helium of about 15 to 20 mm in height was moving as one block over a distance of some millimeters. The small dark pieces made this visible.

In the experiments of this day slight indications of striae near the limit between liquid and solid were seen.

It is an agreeable duty to me to render my cordial thanks to G. J. FLIM, chief of the technical staff, and to L. and A. OUWERKERK, technicians to the cryogenic laboratory, for their intelligent aid.

Mathematics. — *"Projection of the lines in space into pairs of lines in a plane"*. By Dr. HERMANCE MULLEMEISTER. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of February 27, 1926).

Introduction. Since the ordinary space is fourdimensional in lines, and the plane is twodimensional in lines, it is possible to represent the lines in space by pairs of lines in a plane.

If a line l be projected from the centers C_1 and C_2 upon a plane α into the lines l_1 and l_2, this pair of lines will be called the image of l.

Conversely: two arbitrary lines l_1, l_2 in α will in general determine one line l, which is the intersection of the planes $C_1 l_1$ and $C_2 l_2$.

1. The lines in space (∞^4) are the intersections of the planes in the sheaf on C_1 (∞^2) with those in the sheaf on C^2 (∞^2). Each of these sheaves intersect α in ∞^2 lines.

A line l in space is represented by the two lines l_1 and l_2 in which the planes $C_1 l$ and $C_2 l$ meet plane α.

In case l lies in plane α, l_1 and l_2 will coincide with l, and conversely, a line in α, paired with itself ($l_1 \equiv l_2$), is the image of this line itself considered as ray in space.

Two lines l_1, l_2 in α will in general determine a unique line l: the intersection of $C_1 l_1$ and $C_2 l_2$.

An exception will occur, if l_1 and l_2 coincide and this line passes through C_0, the point where $C_1 C_2$ meets α. In this case the planes $C_1 l_1$ and $C_2 l_2$ coincide, l and $C_1 C_2$ (Call this line f) will intersect and l is indeterminate in the plane $fl_{1(2)}$.

Therefore every line l which meets f, has for its image two coincident lines, being the intersection of α and the plane fl.

Conversely, every line in α, passing through C_0, may be considered as the image of *any* ray in $\lambda \equiv fl$. If we let λ revolve about f, its intersection with α will describe a flat pencil on C_0.

The system of rays (∞^3) which meet f (an axial complex having f for its axis) is thus projected into the flat pencil on C_0, every line of which is the image of a field of rays.

The line f has for its image *any* pair of lines through C_0, i.e. any line l_1 through C_0 paired with any line l_2 through C_0. Since it has ∞^2 images, the line f will be called a *fundamental line*.

Every line l through C_1 is *singular* (having ∞^1 images). There are ∞^1 planes through l and C_1; only one plane is determined by l and C_2.

This plane (fl) will meet α in $L_0 C_0$, where L_0 is the intersection of l and α.

The pencil of planes on l cuts α in a flat pencil on L_0, and l has for its image: $C_0 L_0 \equiv l_2$ paired with *any* line l_1 through L_0.

Similarly, every line l through C_2 is singular. One of these singular rays, $C_1 C_2$, is fundamental.

2. *Image of a flat pencil* (l) in a plane μ with vertex M.

Let P_1 be the intersection of MC_1 and α.

and P_2 the intersection of MC_2 and α.

Let l be any ray of the given pencil M.

The projecting planes $C_1 l$ and $C_2 l$ will meet α along the lines $P_1 L_0$ and $P_2 L_0$, where L_0 is the intersection of l and α, which will, of course, lie on the intersection m of the two planes α and μ.

The image of the pencil (l) will thus consist of two *perspective pencils* (l_1) and (l_2), whose corresponding rays meet on the intersection m of α and μ.

The centers P_1 and P_2 of the pencils (l_1) and (l_2) are collinear with C_0; the line $P_1 P_2$ is self-corresponding in the perspectivity and is the image $(l_1'' \equiv l_2'')$ of l'', this being the ray in the given pencil which meets f. (passing through C^* where f intersects the plane μ).

The projecting planes constitute two perspective axial pencils through $C_1 M$ and $C_2 M$, which cut α in the perspective flat pencils P_1 and P_2.

Conversely, two perspective flat pencils in α, whose centers P_1 and P_2 are collinear with C_0, will always be the image of a flat pencil, whose center M is found at the intersection of $P_1 C_1$ and $P_2 C_2$, and whose plane is the plane connecting this point M with the axis of perspectivity m.

If, in a special case, $\mu // \alpha$, m moves off to infinity and corresponding rays of the perspective flat pencils are parallel.

3. Two projective flat pencils (l_1) and (l_2) in α with vertices P_1 and P_2, which are not perspective, are the image of a *quadratic ruled system*, whose axes r_1 and r_2 pass through C_1 and C_2.

Indeed $P_1 C_1$ and $P_2 C_2$ are the axes of the projective axial pencils consisting of the planes which connect the pencil rays (l_1) with C_1 and (l_2) with C_2. These axes do not intersect since $P_1 P_2$ is not coplanar with $C_1 C_2$.

The two projective axial pencils therefore generate a quadratic ruled system whose rulings rest upon the axes $P_1 C_1$ and $P_2 C_2$.

The projective flat pencils (l_1) and (l_2) will generate a conic which is the intersection of the ruled surface with α.

The plane through r_1 and f passes through C_2, and therefore contains a ruling b of the system, whose image is the pair $B_0 P_1$ and $B_0 P_2$, corresponding rays in the pencils P_1 and P_2, such that $P_1 P_2$ does not pass through C_0.

4. *Image of a quadratic ruled system* in general position.

Let $(l)^2$ be a quadratic ruled system which does not pass through C_1 and C_2.

This system will be projected from C_1, by the tangent planes of a quadratic cone, and these will cut the plane α in a system of lines $(l_1)^2$ enveloping a conic.

In the same manner will the ruled system be projected from C_2 into a system of lines $(l_2)^2$ which envelop another conic.

The image of the ruled system therefore consists of two projective line conics in α.

In the ruled system there are two lines which rest upon f; each one of these has for its image two coincident lines $l_{1,2}$ through C_0.

This means that the two conics have two common tangents through C_0, which are coincidences of the projective line conics.

5. *Image of a line-field* $[l]$ in a plane β.

The planes projecting a given line-field $[l]$ from C_1 intersect α in a line-field $[l_1]$ in α, and those projecting $[l]$ from C_2 produce another line-field $[l_2]$ in α, whose lines are in (1,1) correspondence with the lines of $[l_1]$.

The coplanar line-fields $[l_1]$ and $[l_2]$ are not only projective, but also perspective, and have the intersection $^{\alpha}/_{\beta}$ as axis of perspectivity and C_0 as center of perspectivity.

The pencil on C_0 consists of double lines $(m_1 \equiv m_2)$ and is the image of the pencil in β whose vertex is C^*, the intersection of C_1C_2 and β.

The intersection $^{\alpha}/_{\beta}$ also is a double line of the collineation; considered as a line l in β, it coincides with its image $(l_{1,2})$.

Let a second line-field be given in a plane γ, which cuts β in l', then the image of this one again consists of two perspective line-fields in α which also have C_0 as center of perspectivity, and whose axis of perspectivity $^{\alpha}/_{\gamma}$ intersects $^{\alpha}/_{\beta}$ in L_0', where l' passes through α.

6. *Image of a line-sheaf* $[l]^*$ on a vertex O.

Let P_1 and P_2 be the points where the lines OC_1 and OC_2 pass through α, then P_1 and P_2 will, of course, be collinear with C_0.

The line-sheaf on O has for its image the ∞^2 pairs of lines formed by pairing any line of pencil P_1 with any line of pencil P_2. Any such pair determines a ray of the line-sheaf on O.

A part of this line-sheaf is the flat pencil on O in the plane OC_1C_2, whose image is the double line $P_1P_2(l_{1,2})$.

Let a second line-sheaf on S be pictured in the ∞^2 line pairs on Q_1 and Q_2, the points where SC_1 and SC_2 pass through α.

The two line-sheaves on O and S have only one line in common, whose image is the pair P_1Q_1 and P_2Q_2.

7. *Image of a bilinear congruence* [1,1] with directrices r and s.

A line l_1 in α determines a line l of the congruence which is found as the line joining the points in which the plane $C_1 l_1$ cuts the axes r and s.

The plane joining l and C_2 then determines the corresponding l_2.

If l_1 describes a pencil on P_1, the plane $C_1 l_1$ will describe an axial pencil on $C_1 P_1 \equiv p$. The line l will then generate a ruled system on r, p and s.

The plane $l C_2$ will therefore envelop a quadric cone which has among its tangent planes $C_2 r$, $C_2 s$ and $C_2 t'$, where t' is the transversal through C_1 on r and s, resting at X and Y.

The line l_2 will then envelop a conic $\mu_2{}^2$ in α which is tangent to r_2, s_2, $t_2{}'$, the intersections of the above named tangent planes with α.

To the pencil (l_1) on P_1 corresponds a conic $\mu_2{}^2$ generated by its tangent lines (l_2).

In the same way it can be shown that to a pencil (l_2) corresponds a conic $\mu_1{}^2$ generated by its tangent lines (l_1).

The point-field P_1 in α, each point of which may be considered as vertex of a pencil (l_1), is thus transformed into a net of line conics $\mu_2{}^2$, all of whose members are tangent to r_2, s_2 and $t_2{}'$.

The line conic $\mu_2{}^2$ is degenerated, if the pencil vertex P_1 is situated on one or two of the lines r_1, s_1 or $t_1{}''$ (where t'' is the transversal through C_2 on r and s, resting at U and V).

If P_1 is on r_1, the corresponding line conic $[l_2]$ consists of a pencil P_2 (vertex on r_2) together with pencil Y_2.

If P_1 is on s_1, the corresponding line conic $[l_2]$ consists of a pencil P_2 (on s_2) together with pencil X_2.

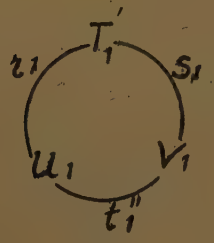
If P_1 is on $t_1{}''$, the line conic $[l_2]$ consists of a pencil P_2 (on $t_2{}'$) together with pencil $T_2{}''$.

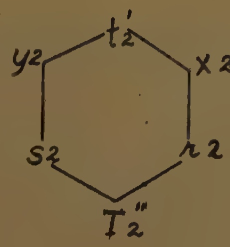
If P_1 is at $T_1{}'$ (r_1/s_1), the only corresponding l_2 is $X_2 Y_2 \equiv t_2{}'$.

If P_1 is at V_1 $(s_1/t_1{}'')$, the only corresponding l_2 is $X_2 T_2{}'' \equiv r_2$.

If P_1 is at U_1 $(r_1/t_1{}'')$, the only corresponding l_2 is $Y_2 T_2{}'' \equiv s_2$.

The following diagram shows the dual relation between the points and lines of triangle $T_1{}'\, V_1\, U_1$ and the triangle formed by $t_2{}'\, r_2\, s_2$.





indicating that:

Any l_1 along r_1 has corresponding l_2 through Y_2
" " " s_1 " " " " X_2
" " " t''_1 " " " " T''_2

and also:

Any l_1 through T'_1 has corresponding l_2 along t'_2
" " " V_1 " " " " r_2
" " " U_1 " " " " s_2

and vice versa.

The results which are here summarized follow from the consideration of lines and planes in space, and can be verified by a construction in the plane α, since every space construction for finding the l_2 corresponding to a given l_1 may be replaced by a plane construction in the plane α.

Astronomy. — *"Report on the expedition to Sumatra for observing the total solar eclipse of 1926 Jan. 14th."* By J. VAN DER BILT, M. G. J. MINNAERT, W. J. H. MOLL and A. PANNEKOEK.

(Communicated at the meetings of October 31, 1925 and June 26, 1926)

I. *Organization and instrumental outfit.*

In the spring of 1924 the Royal Academy of Sciences appointed a committee which, after the nomination of some members from outside the Academy, consisted of Messrs J. VAN DER BILT, E. VAN EVERDINGEN, E. HERTZSPRUNG, W. H. JULIUS, M. G. J. MINNAERT, W. J. H. MOLL, J. J. A. MULLER, A. A. NIJLAND, A. PANNEKOEK, P. J. VAN RHIJN, W. DE SITTER and J. P. VAN DER STOK. This committee, on April 5th 1924, discussed the eclipse-problems thought most important and the general way along which they might be studied. At the following meeting, December 13th 1924, it was reported that the necessary funds for an expedition would be available; the members VAN DER BILT, MINNAERT, MOLL and PANNEKOEK were asked to form the observing party and, with the president of the committee, to act as an executive committee of the expedition. Unfortunately we could only for a short while enjoy the expert advice of our president Prof. Dr. W. H. JULIUS, who died on April 15th 1925 ; but we were able to draw up the general lines of research under his direction.

Thanks to Messrs NIJLAND and ORNSTEIN we were able to do all the preparatory work in the Astronomical Observatory and the Physical Laboratory of the University at Utrecht. The executive committee engaged Miss J. C. THODEN VAN VELZEN, a candidate for the Doctor's degree, as assistant, her duties to begin on May 1st 1925. Mr. H. C. BURGER, Lector in Physics at the Utrecht University has greatly obliged the Committee by giving his valuable advice in many difficulties.

The expedition was organized entirely through private gifts and facilities. The important gift of 30.000 guilders from a resident of Amsterdam, which made the expedition at all possible, has been already announced at the meeting of the Royal Academy on December 27th 1924. It was followed by a gift of 5000 guilders from the „Bataafsche Petroleum Maatschappij", which, moreover, invited the observing party to its estate at Pladjoe near Palembang. Our assistant was enabled to join the expedition through funds from the „Ondernemersraad voor Nederl. Indië", the „Nederlandsche Handel Maatschappij", the „Koloniale Bank" and the „Deli Batavia Maatschappij". The Directors of the Navigation Companies „Nederland", „Rotterdamsche Lloyd" and „Kon. Paketvaart" allowed a free transport of the instruments and a reduction of 50 % to the personal passage.

Observing place.

The zone of total eclipse ran across Sumatra, Bangka and Borneo with a gradual decrease in the duration of totality. The central line on Sumatra ran South of Bengkoelen, over Tebing Tinggi and North of Palembang.

We were advised by employees of the „Bataafsche Petroleum Maatschappij" to build our camp near the coast or in the plains, at a sufficient distance from the mountains; observations concerning the gathering of clouds, which the Resident of Palembang, at our request, ordered to be made at different stations in January 1925, pointed in the same direction. In the neighbourhood of the mountains the chance of a clear sky proved to be much less than that along the coast, for which at the hour of total eclipse (2h. 30m. p.m.), the estimate was about 40 %. Though at Bengkoelen the chance for clear weather was a little more than at Palembang and the duration of total eclipse a little longer, we chose the neigbourhood of Palembang, on the ground that our instrumental outfit needed the vicinity of a well-equipped city; as such Bengkoelen stands decidedly behind Palembang. The hospitality offered by the „Bataafsche Petroleum Maatschappij" definitely settled our choise, since it would put the numerous technical facilities of Pladjoe at our disposal. So we decided to build an observing-camp on the central line near Talang Betoetoe, that seat of a Government official (Controleur), about 15 kms North West of Palembang. An additional advantage of this choice was that — most of the other parties having decided for Bengkoelen — it prevented the crowding of all the observers on a single spot of the central line.

Observing program.

In drawing up a programme of observations we thought it best to restrict ourselves to problems raised by the result of modern theoretical investigations.

Of these, the problem of the corona is doubtless the most important. Its spectrum consists of a continuous background with a number of bright lines. The first is probably formed by reflected sunlight and light from the corona itself; this is suggested by the fact that the Fraunhofer lines are weaker than those of the solar spectrum. A quantitative comparison of these two continuous spectra of the corona may add to our knowledge of its constitution.

As to the bright-line spectrum of the corona, not a single line of it is represented in the spectra of known elements. The best working hypothesis is to ascribe these lines to atoms with an abnormal number of electrons, i.e. to a multiple ionization of the atoms. The lines have not yet been reproduced in the laboratory; so their wavelengths are uncertain and suggestions as to their origin, based upon their numerical relations could neither be proved nor disproved. Our knowledge, then, must be drawn from a study of the corona itself. For this it would be needful to get as many lines as possible and to measure their wavelengths with the highest precision. This will also enable us to judge of the reality of a number of doubtful lines, observed on a single occasion; and it will teach us — when duly repeated at future eclipses — whether the corona spectrum is variable or not. In the third place it is important to study the distribution of light in monochromatic images of the corona produced by different lines; this may teach us, which of them originate from the same kind of atoms and which from different kinds.

The spectrum of the chromosphere, too, must be observed from a modern point of view. The theory of ionization has emphasized the importance of accurate values for the intensities of the different lines of the same element. The great intensity of the enhanced lines suggests that in the outer atmosphere of the sun the atoms are more ionized than in the layers, which, by their absorption, yield the Fraunhofer spectrum. Thus also a variation of the ionization with increasing height may be expected. There exist, however, no reliable quantitative data about line-intensities. On the photographic plate a difference in intensity shows itself as a difference in the density of the silver deposit, which can be measured with a microphotometer. For the reduction of densities to intensities and for the interpretation of a change in intensity along each line, we must have some comparison line-spectra, weakened in a known ratio. Moreover, in order to compare the lines in different spectral regions, some standard-spectrum of known distribution of energy must be photographed on the same plate.

The usual flash-spectra obtained with a prismatic camera are not adequate to this investigation, because the light-source is an arc of the chromosphere of unequal width, and consequently the blackness of its image will depend not only on its intensity but also on the width of the arc. Therefore, in order to get accurate intensities, the spectrograms must be taken with a slit-spectrograph.

The continuous corona spectrum.

For the measurement of the intensities of the Fraunhofer lines, no great dispersion is wanted. For the sake of an increased brightness, a small dispersion together with a large angular aperture may be recommended. The two prism-spectrograph, built for the eclipse of 1901 seemed very appropriate for this purpose. The solar image is formed by an objective of 10 cm. with a focal length of 38 cm. The objectives of the collimator and the camera have a diameter of 36 mm. and a focal length of 13 cm.; the two compound prisms are 60 mm. wide and 38 mm. high. Upon examination, the prisms proved to give bad images, chiefly caused by large striae in the Canada balsam; these prisms were re-polished and freshly cemented by the firm of CARL ZEISS, and after this they gave very good images.

In their report on the observation of the eclipse of August 21th, 1914, Messrs MIETHE, SEEGERT and WEIDERT have given a description of the spectrograph, with which they intended to photograph the continuous corona spectrum. In this instrument the focal ratio of the diameter of the camera-objective is only 1 : 2, and it, therefore, seemed to serve our purpose even better than our own spectrograph. The director of the GOERZ Works most kindly and disinterestedly lent us this instrument. We decided to compare the corona-spectrum which it would yield, with a number of comparison spectra, obtained by mixing sunlight and artificial white light in various known proportions.

The bright line-spectra of the corona and the chromosphere.

For the observation of these spectra we intended to use two spectrographs. One was the three prism-spectrograph, built for the eclipse of 1901 and described in the reports on that eclipse. The solar image is formed by an objective of 80 mm. with a focal length of 61 cm ; the objectives of the collimator and the camera have a diameter of 55 mm and a focal length of 42 cm. The compound prisms are 60 mm wide and 55 mm high.

With this instrument, too, the prisms, at first, gave bad images. The ZEISS firm did not succeed in fully correcting these prisms, but they were so far improved as to yield very satisfactory images. We intended to place the slit along the East-West diameter of the solar image ; thus, we got on both sides of the moon a radial section through the corona, nearly coinciding with the direction of the sun's equator. The plate would contain an iron-arc comparison spectrum, adjusted so as to get the iron lines only across the dark lunar disk and outside the corona.

The second instrument, with which we planned to photograph the spectrum of the corona and the chromosphere, was originally a large prismatic camera, built by Messrs TROUGHTON, COOKE and SIMMS for the eclipse of 1901. For our purpose we had it changed into an auto-collimating slit-spectrograph (Littrow-adjustment) ; its excellent TAYLOR-triplet (aperture 16 cm; focal length 260 cm.) now being at the same time collimator and camera objective. One of the two 45° prisms proved to give very bad images, probably the result of internal strains. We, therefore, ordered from COOKE a third prism of the same dimensions. At the same time, the rejected prism was sent to the SCHOTT Glass Works at Jena to be submitted to a renewed process of annealing and cooling (Präzisionskühlung) after which it was ground again at the ZEISS Works. The result was quite satisfactory ; after its return the prism showed about the same qualities as the other ones and therefore all three were mounted in the new spectrograph.

We planned to observe the corona spectrum and the 1st and 2nd flash on plates, which would also contain iron-arc comparison-spectra for accurate wavelengths of the corona-lines and for reliable intensities for those of the chromosphere. At either contact a number of exposures would be made. For this purpose 12 plates were to be adjusted at the surface of a rotating cylinder. A solar image would be formed on the slit of this instrument by the STEINHEIL photographic objective belonging to the Utrecht Observatory; this has a diameter of 26 cm and a focal length of 345 cm.

In order to get the successive layers of the chromosphere with maximum extension on the slit, the latter must be tangent to the solar image at the point of contact.

The relative positions of solar image and slit must remain exactly the same during the observations. A rotating coelostat is generally used for this purpose, but such an arrangement could not fulfil our requirements. The sun's image was not allowed to shift its position relative to the slit more than 1 or 2 seconds of arc, whereas the displacements, due to the imperfection of the usual coelostats and siderostats proved to be 5 to 10 seconds. Even an exceptionally well built coelostat, which was offered us by Prof. MIETHE at Charlottenburg, showed oscillations of the image, which were quite unallowable. In order to escape from these difficulties, we have chosen a fundamentally different arrangement. This consists in clamping the coelostat mirror and moving the objective in the opposite direction in which the image would travel in case of a stationary lens. If, then, the speed of the lens is made to equal that of the moving image, this will be kept in a fixed position. The screw, moving the lens, will have its errors, as well as that of the coelostat. But the effect of these errors on the steadiness of the image will be much less. In fact, compared with that, due to the coelostat-errors, it will be as many times smaller as the radius of the wormwheel is contained in the focal length of the lens. In our case this ratio is about 25. With a screw of the same quality as used in the coelostat, we, therefore, may expect the displacements of the sun's image to be much below one second of arc. The screw moves the lens by way of a small electro-motor, properly geared down, and regulated by a clock ; a scheme, designed by GERRISH for driving the telescopes at the Harvard Observatory. In this way the sun's image will be kept in the same steady position for both the 1st flash and the corona ; the coelostat-mirror will then be turned over an accurately determined angle for the second flash.

Monochromatic images of the corona.

In order to obtain the distribution of the radiation in the corona for various wavelengths, the use of a prismatic camera is indicated ; this will yield a number of monochromatic images of the corona. The usual prismatic cameras having all been designed for the flash spectrum, we had to discuss the demands for work on the corona. The inner-corona sends us some faint monochromatic radiations and a rather strong continuous spectrum. The surface-brightness of the monochromatic corona images depends on the angular aperture of the camera ; the contrast between these images and the continuous spectrum depends on the dispersion of the prisms. Hence, both the angular aperture of the camera and the dispersion had to be taken as large as possible. According to this principle we designed two prismatic cameras of a special type.

The first one has a camera with a ZEISS Astrotriplet, with an aperture of 6 cm and a focal length of 27 cm, making the inner diameter of the corona-rings 2.4 mm. In front of this objective are four flint prisms of 66° ; they give a dispersion of 5°,5 from H_β to H_γ. With such a long path inside the prisms, there is a danger that light-beams, far away from the central one, will partly be cut off ; this was compensated by increasing the size of the prisms as they came farther from the camera. As a result of the strong astigmatism caused by such a series of prisms, the corona-ring is circular only for the central wave-length ; for the shorter waves the rings are elongated in the direction of the spectrum ; for the longer waves they are elongated perpendicular to the spectrum. Since the camera would be in the way of the incident light, we placed a small mirror in front of the first prism. This mirror sends the light reflected from a coelostat-mirror through the train of prisms. The instrument was constructed in the ZEISS Works at Jena.

In our second prismatic camera we used a liquid prism. As a consequence of the great dispersion of highly refractive liquids, a single liquid prism will give a dispersion equal to that of a number of glass prisms. Such prisms find no application in research work, because small differences of temperature cause striae in the liquid, which may distort the spectral images. By seeing to good isolation, we hope to prevent rapid changes of temperature. The same intention led us to the use of a direct-vision prism ; the thick pieces of glass in front and behind the liquid, help to protect it from the heat. Since the instrument will only be exposed when the sun is eclipsed, the heating by the radiation itself will be negligible.

We, therefore, ordered from Messrs STEEG und REUTER at Homburg v. d. Höhe, a direct-vision "WERNICKE"-prism, to be filled with ethylcinnamate. We intend to use this in combination with a ZEISS camera of the same type as used in the last mentioned instrument.

We have thought it an interesting experiment to see whether, in eclipse-work, such a peculiar prismatic camera could be useful.

Solar radiation.

ABBOT derived the distribution of the energy over the sun's disc by direct measurements in a solar image. These do not include more than 95 % of the radius, reckoned from the centre, whereas just the sun's edge, from which comes all the radiation, emitted under angles of 72° to 90°, is of fundamental importance to our knowledge of the physical constitution of the photosphere.

JULIUS remarked that measurements in a solar image will not give correct results, since it is covered by light, diffused by the earth's atmosphere. He, therefore, proposed a method to deduce the distribution of intensity from measurements of the radiation during a solar eclipse. This method, which is entirely free from the disturbing effect, just mentioned, has been applied at the eclipses of 1905 (Burgos, Spain), 1912 (Maastricht, Holland)

and 1914 (Hernösand, Sweden); on the last occasion for a number of spectral regions.

The results of the 1914 eclipse, however, showed that the method is only reliable just before and after totality, i.e. when observing the radiation of the outermost regions. We originally planned to apply JULIUS' method, thus limited, at the Sumatra-eclipse. But since this eclipse did not seem to serve the purpose very well (difference between the solar and lunar diameter rather large; a damp, tropical climate) we resolved to try measurements outside an eclipse, using refined instruments and choosing the most favourable observing site. As such we decided for the Gornergrat, Switserland; Messrs MOLL, BURGER and VAN DER BILT spent the month of August 1925 up there and got a series of preliminary measurements, the results of which have been published in the Bulletin of the Astronomical Institutes of the Netherlands (Vol. III N⁰. 91). Measurements during a solar eclipse following JULIUS' suggestion remain desirable, even now, but only at an eclipse of short duration, observable in a good climate.

II. *The expedition to Sumatra.*

The journey.

The observing party left Marseilles for Singapore on the „Rotterdamsche Lloyd" liner „Tabanan", November 10th 1925. From Singapore the ss „van Swoll" of the „Koninklijke Paketvaart Maatschappij" conveyed the expedition to Palembang, where it arrived on Dec. 4th. A few hours earlier the ss „Wega" of the Colonial Service Marine, put at our disposal by the Vice-admiral, Commander in chief of the naval forces at Batavia, had been anchored on the river. Its commanding officer, Mr. J. M. VOOREN and his staff, enlarged at our request with two additional officers, have regularly taken part in the mounting of the instruments, in the drills and the observations. The „Wega" had also brought to Palembang Mr. N. P. MIEDEMA, chief-instrumentmaker in the Topografic-Service of the Army; we are much obliged to the chief of this Service for sending us this officer, whose zeal and capability have been of great value to us. On Dec. 31st Messrs P. VAN LEEUWEN BOOMKAMP and L. E. VAN LEEUWEN BOOMKAMP joined the party and at once took part in the work.

The members of the expeditions gladly accepted the invitations from the Directors of the „Bataafsche Petroleum Maatschappij" to live in cottages of the Pladjoe-estate and from the Commander of the Navy to use the first class cabins of the „Wega". Two days after the eclipse, the whole party left Palembang for Batavia on this ship. From there, Mr. PANNEKOEK went straight to the „Bosscha Observatory" at Lembang in order to continue his observations of the southern Milky Way, which he had already started during the outward trip. The other members spent a few days in Batavia; there they payed their respects to Their Excellencies the Governor General and the Commander in chief of the naval forces, and thanked them for the courtesies and assistance which all the various government services had extended to the expedition. Mr. P. VAN LEEUWEN BOOMKAMP then, invited them for a short stay in Java (including a visit to the Bosscha Observatory) and in Deli (East-coast of Sumatra). From there they returned in Holland on Febr. 14th 1926 in the Nederland-liner „Koningin der Nederlanden". Mr. PANNEKOEK left Java in the same ship on May 19th.

The eclipse-camp.

Prof. E. W. BROWN of Yale University had informed us that, judging from the 1925 eclipse-results, the central line on Sumatra would run about half a mile north of the almanac-line. We, therefore, choose for the installation of our instruments, a site about 18 kms from Palembang, by the road from Talang Betoetoe to Pangkalan Benteng. The coordinaties of this place were

$$\text{Latitude} = 2^\circ\,52'\,58'' \quad \text{South}$$
$$\text{Longitude} = 6^h\,58^m\,40^s.2 \quad \text{East}$$

After the brush had been cut and the ground cleared, the "Bataafsche" started with the building of our camp according to our instructions. They had put their architect Mr. B. C. VAN DE WETERING in charge of the work; he finished it promptly to our entire satisfaction. The relative position of the piers is shown in the diagram; over these piers we had shelters, the upper part of which could be removed when the observations made this necessary.

To the North of the piers a large barrack was built, which contained a dark room, a workshop, a dining room, a packingroom, and a garage. Through the care of the Chief Engineer of the Civil Public Works, the camp was surrounded by a barbed wire railing. Outside this railing barracks were built for a non-commissioned officer and seven soldiers, who by order of the Military Officer in command, would have to guard our camp.

About 100 m. from the piers a gasmotor and dynamo were installed; the latter supplied the current for two electric arc-lamps, the storage batteries, the illumination of the dark room and a number of dim lamps near the instruments. The storage batteries were lent to us by the „Borneo Sumatra Handel Maatschappij" and charged by the „Nederlandsch Indische Gas Maatschappij".

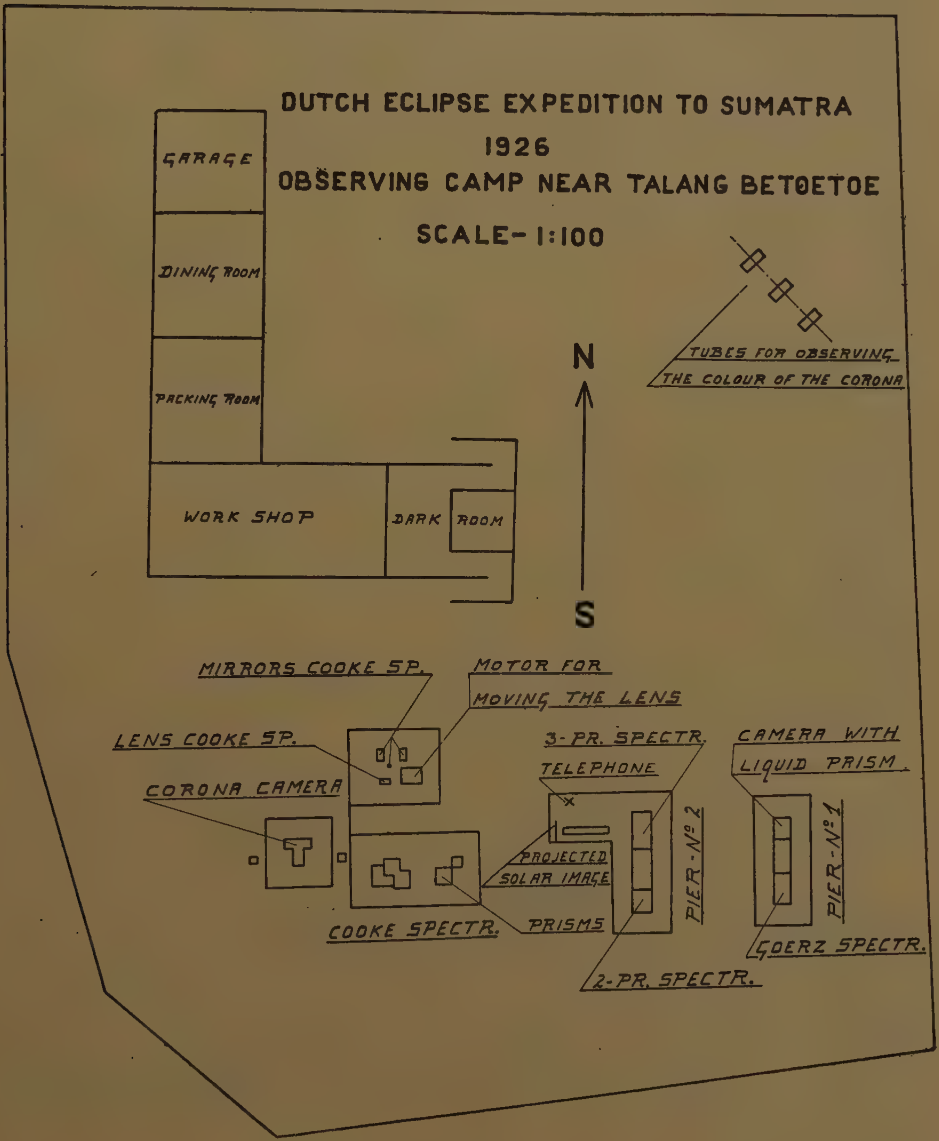
A motor-launch and a motor-car, both of the „Bataafsche" secured a regular communication between Pladjoe, Palembang and the eclipse camp.

The instruments.

1. *Adjustment.* As indicated in the diagram, the prismatic camera with liquid prism and the Goerz-spectrograph were fed by the mirrors of the Eastern-most siderostat; this was a double polar siderostat, clockdriven. The two- and three-prism spectrographs were fed by the mirrors of the second siderostat; this too, was a double polar siderostat, driven by a motor which was regulated by a pendulum-clock.

The mirrors and the spectrographs were adjusted with respect to the pole of the heavens by using two universal instruments, borrowed from Prof. H. J. HEUVELINK of Delft and Prof. J. W. DIEPERINK of Wageningen. With a view to make these adjustments independent of weather conditions, we began with the measurement of the azimuth of a land-mark, a fork in a leafless tree, about 900 m Southward of the camp.

The siderostats and coelostats were adjusted by a method differing from that usually followed. In order to apply this method, both universal instruments had been supplied with a Gaussian eye piece, through which auto-collimation became possible. Now, to adjust the axis of the siderostat



with respect to the pole, one of the mirrors was placed perpendicular to the axis; then a universal instrument was placed in front of the mirror, and its telescope — by way of the known latitude of the camp and the azimuth of the landmark — carefully adjusted so as to be parallel to the earth's axis. We had then only to correct the inclination and the azimuth of the axis of the siderostat, till the observer at the telescope saw the cross-wires coincide with their reflected images.

The spectrographs were adjusted in the following way; the universal instrument was placed on the pier of the spectrograph with its telescope properly adjusted so as to be parallel to the earth's axis, and the mirror adjusted so as to get a solar image on the cross-wires. Then, the driving mechanism of the siderostat was started, the universal instrument exchanged for the spectrograph and the latter adjusted so as to get the solar image on the slit.

With the coelostat used for the corona camera we proceeded as follows: the two universal instruments were placed on either side of the mirror, the telescopes pointing East and West and their optical axes coinciding. Then, by adjusting the mirror in its box and changing the azimuth of the axis of the coelostat, a position could be arrived at, in which the cross wires of both telescopes could be brought into coincidence with their reflected images. This meant that the plane of the mirror was parallel to the axis, and the axis was in the meridian plane. It remained to give the latter its proper inclination; this was done with one universal instrument, whose telescope was in the meridian, and at right angles to the earth's axis. The inclination of the axis of the coelostat was then corrected, till the observer at the telescope saw the wires cover their reflected images.

The method of auto-collimation was again very useful on the day of the eclipse; it allowed the coelostat mirrors, which could not be adjusted in hour-angle, to be clamped in the exact position on starting the driving mechanism.

All the mirrors have been resilvered a week before the eclipse. Mr. G. F. F. AVÉ LALLEMANT, in charge of the hospital at Pladjoe, had the courtesy to abandone his well lighted and dust-free operating room for this purpose.

2. *Focussing.* We devised the following method for obtaining a sharply focussed image on the slit of the spectrograph. A large screen with a central hole of about 1 cm was moved to and fro before the objective; if the slit is not exactly in the focal plane of the lens, the sun's image will be seen either to follow the motion of the screen, or to move in an opposite direction. Since the human eye is very sensitive to small displacements, this method affords a very sharp focussing. With regard to the spectral regions under observation, the use of a blue glass was necessary.

The two prismatic cameras were photographically focussed, using a collimator and an iron arc-lamp. About the camera with liquid prism we want to say that the results came up to our expectations; even without special precautions, the sharpness of the iron lines was very satisfactory. The ethylcinnamate in the brass tube, after some days, showed a slight precipitation and was therefore replaced by fresh liquid one day before the eclipse.

3. *Adjustment of the slit of the large spectrograph.* The mounting of the large auto-collimating Cooke-spectrograph required a number of piers (see diagram).

A mirror mounted as a coelostat sent a highly inclined beam of sunlight in the plane of the meridian to a second mirror, which reflected the light to the Southpoint of the horizon. Thus, the rotation of the sky caused the solar image to travel in a horizontal direction over the slit; this motion, as has been stated above, could be compensated by a horizontal motion of the objective.

The mirrors were clamped in such a position, that two minutes before totality the solar image was 1 cm from the slit and was approaching it. On the instant it reached the slit, the carrier of the lens was coupled to the already working motor, causing the solar image to remain fixed. The observer at the viewing eyepiece of the spectrograph could visually observe the spectrum and move the slit parallel to itself with a micrometer-screw. By the length of the continuous spectrum he could judge what part of the slit covered the sun's image. Practical considerations induced us to adjust the slit parallel to the tangent, 1″ inside the solar image. In this position the slit cut edge of the image 2°.5 from the point of contact in a point, where the chromosphere would be covered by the moon only by 0″.02. This position would be kept while photographing the spectrum of the corona. In order to get the second flash, an assistant could turn the coelostat mirror through a previously determined angle. The moving lens compensated the rotation of the sky and the mirror could be adjusted for the second flash with a precision that left nothing to be desired.

The colour of the corona.

Some days before the eclipse, we decided to have colour observations of the corona made by amateur-observers. The contradictory results to which colour-estimates of the corona have led, are probably due to a lack of a suitable object for comparison. As such we choose a piece of white cardboard, illuminated by a Philips' daylight-lamp. The observer, looking in a cardboard tube could simultaneously view the corona and the illuminated screen and compare their colours. We found Messrs VAN DE WETERING, MOORMANN and WALLIS DE VRIES willing to make these observations.

Time-service.

The Navy Department in Holland, had granted us the loan of 3 chronometers. During our stay at the eclipse camp these were kept under control by comparing them with one of the chronometers of the „Vega", the correction for which was derived from daily wireless time signals. Since the calculated time of the first flash could not be trusted to a few seconds, we took two precautions so as to be exactly in time. Firstly we arranged to have a solar image of about 10 cm projected on a screen and to observe the moment at which the distance between the horns of the crescent was that computed for 12 seconds before totality. Secondly we had a telephonic connection made between the camp and a post on the central line, 10 kms distant. An observer at this point would see totality begin 12 seconds earlier than the observers in the camp. This responsible post was held by Mr. H. J. SCHMIDT, acting Resident of Palembang. His signal was received by Mr. J. VAN DER BILT, who also observed the projected solar-image, and with the assistance of Mr. ADAM, 4th officer of the Government's Navy, counted and called the seconds during the total phase of the eclipse.

Eclipse-day.

A week before the eclipse we decided upon the operations to be carried out on the eclipse-day; during the following days the observers went through regular rehearsals. On the eve of the 14th all the instruments stood carefully adjusted and tested; and we had the agreeable feeling that our rather complicated equipment, every detail of which had been cared for, would fully justify our expectations.

The arrangement for eclipse-day was the following:

a. *Corona camera with liquid prism:* Mr. E. K. VAN MELLE, 2nd officer Governm. Navy.

b. *Goerz-spectrograph:* Mr. A. J. LOUET FEISSER, 2nd officer G. N.

c. *Two-prism spectrograph:* Mr. J. M. VOOREN, Commanding officer G. N.

d. *Three-prism spectrograph:* Dr. A. PANNEKOEK, for the manipulation of the iron-arc lamp assisted by Mr. R. TROOST, 2nd officer G. N.

e. *Cooke-spectrograph:* Dr. M. G. J. MINNAERT, assisted by Mr. P. VAN LEEUWEN BOOMKAMP at the revolving plate-holder and the slit-shutter; by Mr. J. J. NEESSEN, acting 1st off. G. N. at the iron-arc lamp; by Mr. L. E. VAN LEEUWEN BOOMKAMP at the mechanism for moving the lens; and by Mr. B. M. D. FHIJNBEEN, non-commissioned officer of the Army, at the handle for turning the coelostat mirror.

f. *Corona-camera.* Miss J. C. THODEN VAN VELZEN.

Dr. W. J. H. MOLL superintended the correct execution of the program, ready to act in case of emergency. The instrumentmaker, Mr. MIEDEMA stood by him.

Before we left Holland, we had gathered from various informations, that we should encounter a rather regular change of weather in the course of a day, with little chance of a clear sky in the afternoon. But, to our surprise, the weather, during the six weeks of our stay at Palembang, was without any regularity. Entirely cloudy days were sometimes followed by rains, sometimes by sunshine; and this, apparently, regardless of the hour of the day. The last five days before the eclipse, conditions at eclipse-time were rather favorable.

On the morning of January 14th there were thin clouds in the sky. Shortly before noon, denser clouds came over from the North-West, soon covering the whole Western sky; they brought us a shower about half an hour before 1st contact. It looked for a while as if there would be a change for the better; but then a layer of cirro-cumuli began to cover the sun.

The mirrors and the projected solar image could still be adjusted, but towards 2nd contact the sheet became thicker and, though the beginning of totality could be seen with the naked eye, the flash spectrum was not visible in the viewing telescopes of the 3-prism spectrographs. The signal from the observer in the telephone-hut, where the sun was free from clouds, came exactly 12 seconds before totality; the screen had since long ceased to show anything of the sun's image. Totality began two seconds later than was computed. Towards the time of third contact, the sheet of clouds became a little thinner. The observers duly went through all the operations, but were convinced of the fruitlessness of it; development of the plates proved that they were right. The plates taken with the slit spectrographs revealed nothing. On those, taken with the slitless spectrographs, the prominences have left faint traces; the plate of the corona camera showing the $H\beta$, $H\gamma$ and $H\delta$ images and that of the liquid prism camera showing in addition to these, the H and K lines. This fact is an indication of the great light-gathering power of the two instruments. Needless to say, that, in these circumstances, colour-estimates of the corona could not be made.

Final remarks. The expedition had no success; but neither the effort nor the expense have been made for nothing. In the course of the preparative work new problems have been brought forward, new methods have been devised and new instruments have been constructed, which could be tested not only in the laboratory, but also under the peculiar conditions of an eclips-camp in a tropical climate.

This last experience is valuable in view of the eclipses of 1929 and 1934, which will be visible in the Dutch East Indies.

Our expedition, though missing its mark, has not been entirely fruitless. It led to the expedition to the Gornergrat and it offered to Mr. PANNEKOEK an opportunity to extend his researches on the structure of the Milky Way to the whole sky. We consider these two facts to constitute a positive gain to science. Moreover, thanks to the improvement of the older instruments and the construction of modern ones, the Royal Academy now possesses a valuable instrumental outfit, which is not solely useful for future eclipse-work, but, between eclipses, will be available for scientific work of different kind.

In concluding, we wish to express our appreciation and gratitude to

Mr. P. VAN LEEUWEN BOOMKAMP who, feeling sure that the Dutch Government would not be prepared to pay the heavy expenses of a solar eclipse expedition, generously provided the necessary funds, both for the Gornergrat- and the Sumatra expeditions. He thus saved the honour of our national science at an international scientific event.

Furthermore, we are greatly indebted to the Directors of the „Bataafsche Petroleum Maatschappij" and to all the other Companies mentioned in this and in our first report.

We also want to express our gratefulness to all the Government employees; and to all the managers and employees of estates and factories, whom we met on our way; they all did their best to be useful to our work and to make our ocean trips and our stay in India a real pleasure to us all.

Astronomy and Geophysics. — *"Ionisation Equilibrium in Stellar Atmospheres and in the Earth's Atmosphere".* By Prof. A. PANNEKOEK.

(Communicated at the meeting of September 25, 1926)

In 1920 the Bengalese physicist MEGH NAD SAHA derived from the equations of chemical reactions in thermodynamical equilibrium a formula for the ionization as a function of temperature and pressure:

$$\frac{x}{1-x} P_e = \frac{(2\pi m)^{3/2}}{h^3} (kT)^{5/2} e^{-\chi/kT}$$

where x is the fraction of the gas ionized, χ the ionization energy per atom, m the mass of an electron and P_e the electron pressure. This formula has already had an extensive application on the stellar atmospheres and it has provided a physical basis for the explanation of stellar spectra. There remained, however, an uncertainty. The stellar atmospheres are not gases in thermodynamical equilibrium, because a radial stream of energy goes outward causing the temperature to decrease to a boundary temperature. Thus the formula is not strictly applicable to these atmospheres; and where discrepancies are found between observational data and theory it cannot be decided whether this discrepancy is real or should be ascribed to this deficiency of theory.

This uncertainty can now be removed since formulas relating to ionization in non-isothermal gases have been derived, at first by SAHA and SUR, and then by J. WOLTJER [1]), who made use of MILNE's researches. For the unknown mechanisms of ionization by incident radiation and of recombination of an electron with an ion MILNE introduces probability coefficients, which multiplied by the numbers of the particles give the numbers of the processes of ionisation and recombination per second. In a state of equilibrium these numbers must be equal; thus a relation between the numbers of the three kinds of particles is found. Applying this relation to the case of an isothermal gas, we must find the SAHA formula; this condition determines relations between the probability coefficients that have been deduced by MILNE [2]). Now we must assume that these coefficients express atomic properties not depending on statistical distribution quantities such as temperature and pressure. Then they must hold also in other cases, when there is no equilibrium and we may introduce them into the formulas representing these cases.

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[1]) Physica 5, p. 406.

[2]) Philosophical Magazine, (6) 47, p. 209, 1924.

If we put x_1 x_2 y the numbers of atoms, ions, and electrons per unit volume, $I(\nu)$ the intensity of the total radiation of frequency ν falling from all sides on the atoms, the number of ionizations by this radiation may be expressed by $x_1\,\psi(\nu)\,I(\nu)\,d\nu$. This probability coefficient ψ has only values for $\nu > \nu_0$, if $h\nu_0$ denotes the energy of ionization; if the energy $h\nu$ is absorbed from the radiation, the part $h\nu_0$ is used for the ionization and the rest $h(\nu - \nu_0)$ is transformed into translation energy of the electron, amounting to $^1/_2\,mv^2 = h(\nu - \nu_0)$. Thus a continuous absorption band is formed, from ν_0 extending to $\nu = \infty$. The compensating process is the recombination of an electron with an ion by impact; the liberated ionization energy $h\nu_0$ with the kinetic energy of the electron is radiated as a quantum $h\nu = h\nu_0 + {}^1/_2\,mv^2$; thus a continuous emission band appears. The number of recombinations, proportional to the number of ions (assumed at rest) and the number of electrons, which by the partition law of MAXWELL have this velocity v, is given by

$$8\pi\, x_2\, y \left(\frac{m}{2\pi\, kT}\right)^{3/2} e^{-mv^2/2kT}\, \{F(v) + I(\nu)\, G(v)\}\, v^3\, dv,$$

where $F(v)$ and $G(v)$ denote the probabilities of spontaneous and of induced recombinations. If the total numbers of ionizations and recombinations, caused by radiation of all wavelengths, are equal, we have equilibrium. Then

$$x_1 \int_{\nu_0}^{\infty} \psi(\nu)\, I\, d\nu = x_2\, y \int_{\nu_0}^{\infty} 8\pi^2 \left(\frac{m}{2\pi\, kT}\right)^{3/2} e^{-h(\nu-\nu_0)/kT} \{F(v) + I \,.\, G(v)\} \frac{v^2 h}{m}\, d\nu.$$

In the case of isotropic radiation of temperature T, where I is given by PLANCK's formula, this equation must produce the SAHA equation

$$\left(\frac{x_2 y}{x_1}\right)_0 = \frac{(2\pi\, m)^{3/2}}{h^3} (kT)^{3/2}\, e^{-h\nu_0/kT}.$$

In this case the integral signs may be dropped, because for each separate frequency there must be equilibrium between ionization and recombination. In this way relations between $F(v)$ and $G(v)$, and $\psi(\nu)$ are found, which introduced into the equilibrium formula give it the form

$$\frac{x_2 y}{x_1} = \left(\frac{x_2 y}{x_1}\right)_0 \frac{\int \psi(\nu)\, I\, d\nu}{\int \psi(\nu)\, e^{-h\nu/kT} \left(\frac{8\pi\, h\nu^3}{c^2} + I\right) d\nu}$$

where the integrations are taken from ν_0 to ∞. This is the same formula as deduced by WOLTJER.

2. For the integration the function $\psi(\nu)$ is needed. It is not quite

unknown; from the experimental fact that the coefficient of absorption at the limit of the band, i.e. for $\nu = \nu_0$ or $v = 0$ is neither zero nor infinite, MILNE deduces that $Lim\ F(v)/v^2$ for $v = 0$ must have a finite value. The simplified mechanism of electron capture used by EDDINGTON to compute the stellar absorption coefficient causes a strict proportionality of $F(v)$ with v^2. This corresponds to $\psi(\nu)$ being proportional to ν^{-3}. If this proportionality does not strictly hold, the differences become important only for large ν, where I is very small. Thus the result computed with this formula, if not rigidly, will certainly be practically right.

For a stellar atmosphere we compute I from the conditions of radiative equilibrium, for which the SCHWARZSCHILD approximation suffices. This means that I for the directions from the lower half of the sphere is taken equal to black radiation of the temperature T_1, the effective temperature of the sun or the star, and for all directions from above it is taken 0. In equilibrium with this radiation the atmosphere has a temperature $T = T_1 \sqrt[4]{1/2}$. In WOLTJER's formula the second therm I in the denominator, originating from $G(\nu)$, may be neglected for the same reason and in the same cases as the second denominator term in PLANCK's formula; it is only relevant for low frequencies, while here we have to integrate over high frequencies only. The integrals in the above formula now become:

$$\int \psi(\nu)\, I\, d\nu = \int C\nu^{-3} \frac{4\pi h\nu^3}{c^2} e^{-h\nu/kT_1}\, d\nu = \frac{4\pi C k T_1}{c^2} e^{-h\nu_0/kT_1}$$

$$\int \psi(\nu)\, e^{-h\nu/kT} \frac{8\pi h\nu^3}{c^2}\, d\nu = \int C\nu^{-3} \frac{8\pi h\nu^3}{c^2} e^{-h\nu/kT}\, d\nu = \frac{8\pi C k T}{c^2} e^{-h\nu_0/kT}$$

Thus the factor by which the formula of SAHA has to be multiplied, will be

$$1/2\, \frac{T_1}{T} e^{-h\nu_0 (1/kT_1 - 1/kT)}.$$

If we write χ for the ionization energy $h\nu_0$, the formula becomes

$$\frac{x}{1-x} P_e = 1/2\, \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} T_1\, T^{3/2}\, e^{-\chi/kT_1}.$$

Thus we find that the ionization, if computed after the Saha formula not with the atmospheric but with the effective temperature, needs only a constant correction factor $1/2 (T/T_1)^{3/2}$, which in this case is $2^{-11/8}$ 1).

3. In the same way also the ionisation of the upper layers of the atmosphere of the earth may be computed. From the propagation of wireless waves around the spherical earth it has been deduced that the highest layers of our atmosphere are conductive through the presence of a great number of free electrons or ions. The lower limit of this HEAVISIDE

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1) The ionization by electron impacts for such small pressures, after R. H. FOWLER's formula (Philos. Magazine, (6) 47, p. 275), is wholly negligible compared with the photoelectric ionization.

layer is given usually at 90 kms and its electron density at 10^5 per ccm. at least; in the daytime the limit seems to be lower and the whole phenomenon seems to be less regular than by night. In order to explain this layer either ionization by impacts of swift moving particles is assumed, which ejected by the sun penetrate our atmosphere, or photoelectric ionization by the solar radiation. The latter effect can now be computed exactly.

The total radiation falling upon the particles is solar radiation proceeding from $^1/_{184000}$ of the sphere; this fraction will be called β. We assume a single gas with ionisation energy χ and temperature T; the effective temperature of the radiation is T_1. Then we have in the same way as in the former case

$$K = \frac{x^2}{1-x^2}\, p = \beta \cdot \frac{(2\pi m)^{3/2}\, k^{5/2}}{h^3}\, T_1\, T^{3/2}\, e^{-\chi/kT_1},$$

where in the first part the total pressure has been introduced, because the numbers of electrons and ions are equal. The gases to be dealt with are nitrogen, oxygen, and hydrogen, for which the ionization potential for the molecules has to be taken. For nitrogen it is 16.9 after the measures of BRANDT; for hydrogen 16.1 ± 0.2 is given by FRANCK and JORDAN[1]) as an average of determinations by many observers; for oxygen, where 15.5 resulted from the older measures of MOHLER and FOOTE a recent accurate determination by LOCKROW[2]) also gives 16.1. Assuming a temperature -55° ($T = 218^\circ$ K) we find for $\log K$ values -18.65 for N, -17.98 for H and O. Thus in all practical cases x is very small, $1-x^2$ may be taken 1, and for K we may write x^2p.

The energy used for ionizing the molecules is taken from the solar radiation having a frequency higher than $\nu_0 = eV/300\,h$; thus an absorption band is formed, beginning at $\lambda = 730\,A$ (for N) or $= 766\,A$ (for O and H). The absorption caused by the ionization of the higher layers weakens the radiation falling upon the lower layers: therefore the ionization of these lower layers is diminished also, and disappears below a certain limit, when all active wavelengths have been extinguished from the solar radiation. Putting α for the atomic absorption coefficient, N' for the number of atoms per ccm for one atmosphere and a temperature T, we find that a layer of the gas 1 cm thick absorbs the fraction $\alpha N'p$ of the incident light. For the atomic absorption coefficient α a formula has been deduced by MILNE by making use of KRAMERS' computations; by omitting several factors of order zero it becomes

$$\alpha(\nu) = \frac{16\pi^2}{3\sqrt{3}}\, \frac{Z^2 e^6}{c\,h}\, \frac{\chi}{(h\nu^3)}.$$

It has been derived for atoms; since factors of order zero are irrelevant here it may be used also for molecules. Computing its value for the limit of the absorption band $\nu = \nu_0$ we find $\log \alpha = -15.91$ for N, -15.71 for O, -17.56 for H.

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[1]) Anregung von Quantensprüngen durch Stösse (Handwörterbuch der Physik **23**, 749, 757).

[2]) Astrophysical Journal **63**, p. 205 (1926).

The distribution of the ions over different layers of the atmosphere may now be computed. In a layer dh we have $N'p\,dh$ atoms; thus the absorption is $dI/I = \alpha N'p\,dh = -\alpha N'H\,dp$, if with H we denote the aequivalent height of one atmosphere. Then

$$I/I_0 = e^{-\alpha N'Hp},$$

gives the weakening of the active solar radiation. This factor adds to the coefficient β in the ionization formula; the ionization is given by

$$x^2 p = K\,e^{-\alpha N'Hp}$$

and the number of electrons per ccm $n = xN'p$ becomes

$$n = N' \sqrt{pK}\, e^{-1/2\alpha N'Hp}.$$

Introducing the numerical values $\log N'$ (for $T = 218^\circ$) $= 19{,}83$; $\log H = 5{,}82$ for nitrogen, 5,76 for oxygen, 6,96 for hydrogen. and $\log K$ as given above, we have

$$n = [10.51]\sqrt{p}\, e^{-[9.44]p} \quad \text{(for nitrogen)}$$

$$n - [10.84]\sqrt{p}\, e^{-[9.58]p} \quad \text{(for oxygen)}$$

$$n = [10.84]\sqrt{p}\, e^{-[8.93]p} \quad \text{(for hydrogen).}$$ [1]

In the following table the value of $\log n$ has been computed for different values of the pressure p, and the corresponding heights in kilometres have been added.

Number of electrons per ccm.

$\log p$ in atm.	Nitrogen $\log n$	Nitrogen h	Oxygen $\log n$	Oxygen h	Hydrogen $\log n$	Hydrogen h
− 7					− 30	500
− 8	− 5.5	120	− 10	103	+ 3.14	710
− 9	+ 4.81	135	+ 4.68	116	+ 5.97	920
− 10	+ 5.39	150	+ 5.67	129	+ 5.80	1130
− 11	+ 5.00	165	+ 5.32	142	+ 5.34	1340
− 12	+ 4.51	180	+ 4.84	155	+ 4.84	1550
− 13	+ 4.01	195	+ 4.34	168	+ 4.34	1760
− 14	+ 3.51	210	+ 3.84	182		

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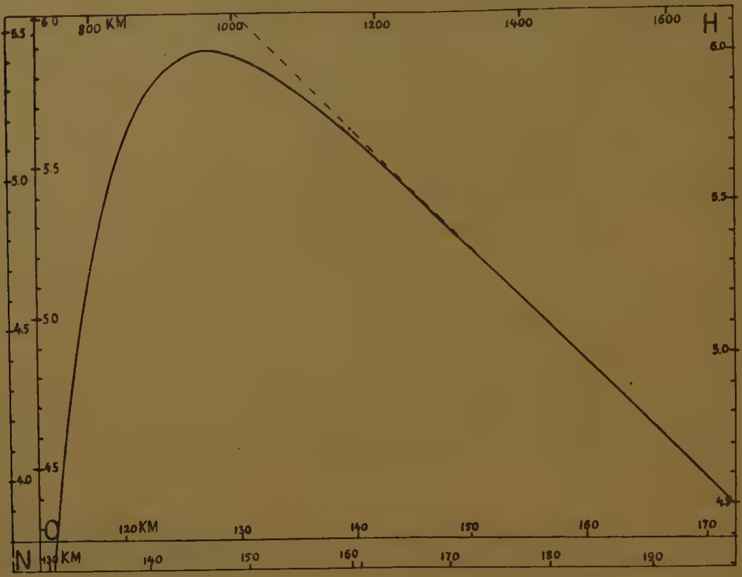
[1] These computations are made for the limit of the band ν_0. For greater values of ν the absorption is smaller, thus the intensity of the smaller wave lengths increases relative to this limit in the lower atmospheric layers. Computation shows, however, that this difference becomes perceptible only in depths where all action has disappeared.

The figure shows the variation of this number *log n* with the height, which for each gas is represented by the same curve, only referred to



different scales, which for each of them has been indicated [1]. The dotted line represents the number of electrons if there had been no absorption. The figure shows that, descending from great heights the number of electrons at first increases regularly, then reaches a maximum between 10^5 and 10^6, and falls rapidly to zero because of the increasing absorption. For nitrogen and oxygen the maximum occurs *at* 145 or 128 kms, the lower limit at 130 and 113 km.

Thus the number of electrons corresponds very well with what has been deduced from wireless experiments. The lower limit, however, found here, lies at a greater height than is usually adopted. Now in the newest literature greater heights are sometimes given; from experiments with short waves TUVE and BREIT deduced heights between 80 and 160 kms. From the experiments of TAYLOR and HULBURT and others HESS concludes: "Die Elektronenzahl pro Kubikzentimeter scheint nach diesen Untersuchungen in Höhen von 110 bis 250 km. ihren Maximalwert (10^5 pro ccm.) zu erreichen (bei Tage)" [2]. According to our computations electrons by photoelectric ionizations cannot occur below 100 kms. A moderate error in the adopted atomic coefficient of absorption has no appreciable influence on log n as a function of p; the value a should be decreased 100 times to lower the limit 30 kms. A lower temperature than —55° C. for the upper atmospheric, however, which contracts the gases more at the bottom of the atmosphere, will diminish the height corresponding to each p appreciably. If the temperature decreases regularly from —55° C. at 15 kms to —160° C. at 90 kms, the lower limit of the electron layer would be brought 30 kms lower. A considerable amount of electrons at a height of 90 kms or lower, in as much as it cannot be ascribed to ionization by impacts, thus points to a much lower temperature of these upper layers than is usually assumed.

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[1] The scale for O should be raised by 0,20; the values used in constructing the figure had been computed with an ionization potential of 15,5.

[2] V. T. HESS, Die elektrische Leitfähigkeit der Atmosphäre, p. 164.

For hydrogen the region of ionization begins only above 700 kilometers. To the HEAVISIDE layer ionization of hydrogen cannot contribute anything. Conversely the ionization of hydrogen at great heights extinguishes all solar wave lengths below 766 A., just the frequencies that are necessary for the ionization of nitrogen and oxygen. The existence of a hydrogen atmosphere above the nitrogen and oxygen atmosphere makes the existence of a HEAVISIDE layer by photoelectric ionization impossible. Therefore, unless this HEAVISIDE layer may be explained wholly by other causes, such as impacts by particles of high velocity, its existence shows, that hydrogen in the usually adopted quantity cannot occur in our atmosphere.

Postscript. From the refraction of sound waves in the higher layers of the atmosphere Prof. E. VAN EVERDINGEN in 1915¹) concluded that the amount of hydrogen in our atmosphere usually adopted is too high; a partial pressure of 10^{-6} at the surface fits better to the observed outer radius of the silent region. This is still too much to allow ionization of nitrogen and oxygen. With a somewhat larger percentage of helium and absence of hydrogen it seems possible, however, to represent the data on the propagation of sound in the atmosphere.

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¹) These Proceedings Vol. 18, p. 933.

Zoology. — *"Castration and implantation of gonads in Xiphophorus Helleri Heckel (Teleost)."* (Preliminary note.) By G. J. VAN OORDT and C. J. J. VAN DER MAAS. (Communicated by Prof. J. BOEKE.)

(Communicated at the meeting of September 25, 1926).

The direct proof of the secondary sex characters of fishes, being influenced by the gonads, has not yet been furnished. However, we assume it on good grounds; we can deduce it a.o. from GERSCHLER's (1914) and BELLAMY's (1922) cross-breeding experiments with *Xiphophorus Helleri* and *Platypoecilius maculatus* ["criss-cross" inheritance of sec. sex characters]. Moreover we can prove it indirectly by BLACHER's investigations (1926), who described several male specimens of *Lebistes reticulatus* with atrophied gonads; in consequence of this fact these fishes lacked some male sec. sex characters (viz. male colouring).

However, the direct proof can only be furnished by castrating or by transplanting gonads in fishes of the other sex.

As far as we know only very few publications on such experiments, which involve many difficulties and a great mortality, have appeared. KOPEĆ (1918) has castrated many specimens of *Phoxinus laevis* Agass., but his results are not very convincing. In the first place because his animals only survived castration 3 weeks at most and secondly because some totally castrated fishes exhibited a nuptial colouring notwithstanding, while in other non-castrated control animals this sec. sex characters did not develop. CHAMPY's attempts (1924, p. 310) to castrate fishes by means of radium rays had no positive results.

So, contrary to Mammals, Birds and Amphibia, the hormonal relation of gonads and sec. sex characters has not yet been demonstrated satisfactorily in fishes. Consequently it is of importance to perform castrations and gonad-implantations in fishes with well-developed sec. sex characters. For this purpose we chose *Xiphophorus Helleri* Heckel, a species belonging to the viviparous Cyprinodontidae, which has been cultivated since 1923 in great numbers by one of us. In this species the ♂ and the ♀ are distinguished by several conspicuous sec. sex characters (cf. VAN OORDT, 1925) of which two male sec. sex characters viz. the strongly elongated caudal fin (the sword) and the anal fin, which has been transformed into an intromittent organ, the gonopod, must be mentioned in the first place.

Adult female specimens of *Xiphophorus* possess a relatively large ovary; attempts to castrate adult ♀♀ had to be given up, because it appeared to be impossible to remove the ovary — the ovaries are originally paired, but soon fuse (ESSENBERG, 1923) — without making too large a wound. Up till now it proved also impossible to implant ovaries or parts of them into the narrow abdominal cavities of ♂♂. So for the present we decided to apply ourselves to:

a. Castration of male *Xiphophorus;*

b. Implantation of testes into female *Xiphophorus.*

We intend soon to pass on to implantation of juvenile ovaries into male specimens of *Xiphophorus* and to injection of gonad-extracts.

a. *Castration of male specimens of Xiphophorus.*

Castration of male specimens of *Xiphophorus* involves many difficulties. In the first half of April 1926 14 specimens were castrated. For this purpose at one side of the body, just above the place where the testis is found — the testis is also originally a paired organ; however, both testes fuse later on to a compact organ, in which the testes can be distinctly distinguished in cross-sections — an incision is made and the testis is carefully removed, without injuring the alimentary tract, which is situated close to the reproductive organs. We always examined microscopically, whether we had removed testis-tissue, because in the neighbourhood of the gonad, especially in large male specimens, much adipose tissue is found, which can only be distinguished macroscopically with great difficulty from testis-tissue. The wound is sewed up with common thread and with the aid of very small chirurgical needles. Generally precautions as to sterility were not taken; we only washed the side of the body to be operated with a weak solution of $KMnO_4$ and the wound was covered with collodium after having been sewed up. Of these 14 specimens only one large adult ♂ survived. This fish, castrated on April 13 1926, was again quite normal after a week; then it swam well and ate much. After having been sewed up, the wound closed totally and gradually became invisible.

Brought together with spec. N⁰. 239 (see below), it behaved as a quite normal male from May to August 1926. The male sec. sex characters remained at the same high grade of development: the fish was also psychically quite normal and tried to copulate with N⁰. 239 again and again. From this it followed that incomplete castration or testis regeneration had taken place. This could only be ascertained by microscopical investigation. The animal was killed on August 20. On autopsy an extraordinarily large testis was found. Microscopical investigation revealed a very active spermatogenesis. The number of spermatozoa is very large, larger than normal; all afferent ducts of the testis are full of spermatophores. Had not this specimen been totally castrated a difference between the old part of the testis and the regenerated part would have been visible. This is not the case, however; only a very small part, situated close to the peritoneum shows a different structure. Evidently the regeneration of the testis has started from this part. Neither has a connection been established between the sperm ducts of the regenerated part of the testis and the ductus deferens.

Similar observations were made by one of us (VAN DER MAAS) in imcompletely castrated cocks. In these animals the testes had also regenerated, appeared to be much larger than normal and the testis-canals were full of spermatozoa. In both cases these phenomena must be ascribed to the fact that the testis was unable to discharge the produced spermatozoa.

b. Testis-implantation in female specimens of Xiphophorus.

In the beginning of April 1926 18 adult female specimens of *Xiphophorus* were implanted with testes of adult ♂♂. The operation was performed by making an oblique longitudinal incision behind the ovary in one side of the body. Through this hole the testis or a part of it in case the testis was very large was cautiously introduced. For the rest we proceeded as described above.

The mortality of the animals operated was not extraordinarily great. On April 16, 6 specimens, swimming normally and eating well, were still living. In these specimens the wound was no longer visible either after some time. On May 13, 1926 one normal looking specimen was killed and investigated but no trace of the implanted testis could be detected. This was also the case in three other spec., killed on June 19. The last remaining spec. (one had died in the meantime) lived till the end of August 1926. This fish, N⁰. 239, a very large specimen, showed a somewhat elongated caudal fin and an anal fin of which the ventral rays were a little longer than normal. These characteristics, which can be compared to male sec. sex characters in the first stage of development, have not necessarily developed under the influence of the implanted testis. As one of us has already communicated the caudal fin of adult female specimens is somewhat elongated (VAN OORDT 1925, p. 47). Moreover, these ventral finrays are a little yellower than the other rays of the anal fin. It appears, however, that in adult ♀♀, still capable of reproduction, the 3d, 4th and 5th ray of the anal fin (for terminology cf. ESSENBERG, 1923) elongates somewhat and grows thicker; consequently they make the impression of a young gonopod in the first stage of development. An accurate comparison of the anal fin of the implanted specimen, above mentioned, with those of normal adult control fishes did not reveal any difference between the anal fins of these fishes.

The testis-implantation has no great influence on the reproduction of the ♀♀. Two months after the operation one of these specimens gave birth to a large number of young. These young were not fully developed, but this is not necessarily a result of the implantation, because it happens also in non-operated ♀♀. N⁰. 239, which had not given birth to young since the operation, died during the birth of its young or shortly after. A number of young were alive and quite normal; the others, however, were not capable of leaving the genital opening of the ♀, this probably causing the mother's death. Owing to this an investigation of the implanted testis could not take place.

Perhaps the fact that in these two cases the young were born late, can be explained by an influence brought about by the implanted testis, for ESSENBERG communicates (1926) that the first sign of sex-reversal in *Xiphophorus* is that the adult females stop to produce young ; in normal cases this takes place almost regularly, each month.

We have seen that operations necessary for testis implantations can be endured with success by adult females. *Xiphophorus* N⁰. 239, which did not differ morphologically from control-specimens, survived operation for nearly 5 months.

From the above it follows that we succeeded in castrating male specimens of *Xiphophorus* and in implanting testes in female specimens of *Xiphophorus*. Some specimens survived operation, the wound healing totally. However, we have not yet been able to demonstrate a hormonal relation between the gonads and the sec. sex characters in *Xiphophorus*. The result obtained justifies us to proceed in the same way in order to demonstrate whether a relation exists between the sec. sex characters and the gonads and if so what the nature of this relation is.

LITERATURE CITED.

BELLAMY, A. W. 1922. Breeding experiments with the viviparous Teleosts, *Xiphophorus Helleri* and *Platypoecilus maculatus* (Günth.). Anat. Record, Vol. **23**, p. 98.

BLACHER, L. J. 1926. Die Abhängigkeit männlicher Merkmale von der Geschlechtsdrüse bei *Lebistes reticulatus*. Trans. Lab. Exp. Biology, Moscow, Vol. **1**.

CHAMPY, CHR. 1924. Sexualité et Hormones. Paris.

ESSENBERG, J. M. 1923. Sex differentiation in the viviparous Teleost *Xiphophorus Helleri* Heckel. Biol. Bull., Vol. **45**.

ESSENBERG, J. M. 1926. Complete sex-reversal in the viviparous Teleost *Xiphophorus Helleri*. Biol. Bull., Vol. **51**.

GERSCHLER, M. W. 1914. Ueber alternative Vererbung bei Kreuzung von Cyprinodontiden-Gattungen. Zeitschr. Ind. Abst. Vererbungslehre, Vol. **12**.

KOPEĆ, S. 1918. Contribution to the study of the development of the nuptial colour of fishes. C. R. Soc. Sciences de Varsovie, Année **11**, fasc. 1.

VAN OORDT, G. J. 1925. The relation between the development of the secondary sex characters and the structure of the testis in the Teleost *Xiphophorus Helleri* Heckel. British Journ. exp. Biol., Vol. **3**.

Zoological Laboratory, University of Utrecht,
Biltstraat 172.

September 1926.

Physics. — "*Methods and apparatus used in the cryogenic laboratory. XIX. The methyl-chloride and ethylene circulations. The hydrogen liquefier and circulation. The helium liquefier and circulation.*" By H. KAMERLINGH ONNES †. Communication N⁰. 158 from the Physical Laboratory at Leyden[1]). (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of September 25, 1926).

§ 1. *The methyl-chloride and ethylene circulations.*

Many years ago a description was given of the methyl-chloride circulation,[2]) but this description no longer completely answers to the reality; the boiling flask in particular has undergone a change that renders it desirable to give a new illustration of this apparatus (fig. 1).

The ethylene circulation, although it has been in use for a great number of years, has never been described in these Communications. It is true that in the excellent article by Prof. MATHIAS in the "Revue générale des Sciences" of 1896 there is a short account and also a drawing of the apparatus at that time, but this account does not answer to the present conditions. A drawing of the ethylene boiling flask, by far the most important part of the circulation, is found in fig. 2. These two drawings speak so plainly for themselves that we believe a very brief description will be sufficient.

The methyl-chloride boiling flask (fig. 1).

The whole upper part of the boiling flask is the same as in the description given in the Communication quoted.

The lower part (beneath the narrowing) to which the drawing refers has been changed. The construction was made simpler and more compact. The liquid methyl-chloride was admitted along *A*; it boils in the chamber *B* (under a pressure of about 2 cm) and the vapour escapes through the upper part of the flask. *C* is a tube which opens into *B* and which serves for the emptying, cleaning, etc. of the apparatus. The compressed ethylene comes into the flask by a spiral in the methyl-chloride vapour-chamber and finally in *F* (in the liquid methyl-chloride); it leaves the flask as liquid at *G*.

The ethylene spiral has a side tube *I*; this is provided with a safety apparatus, consisting of a copper plate *J* which breaks down when for any reason the pressure in the spiral tubes becomes too great and therefore dangerous.

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[1]) As early as 1922, Prof. KAMERLINGH ONNES planned this publication, but much and various work during the last years of his life prevented him from carrying it out. When death overtook him in February of this year it was partly ready, but neither drawing nor manuscript were ready for press. The working up of his notes now published, is done by Prof. Dr. J. E. VERSCHAFFELT of Ghent and Dr. C. A. CROMMELIN of Leyden.

[2]) These Proceedings 6, 668, 1903; Comm. Leyden N⁰. 87.

The ethylene spiral has an inner diameter of 8 mm, an outer one of 10 mm.

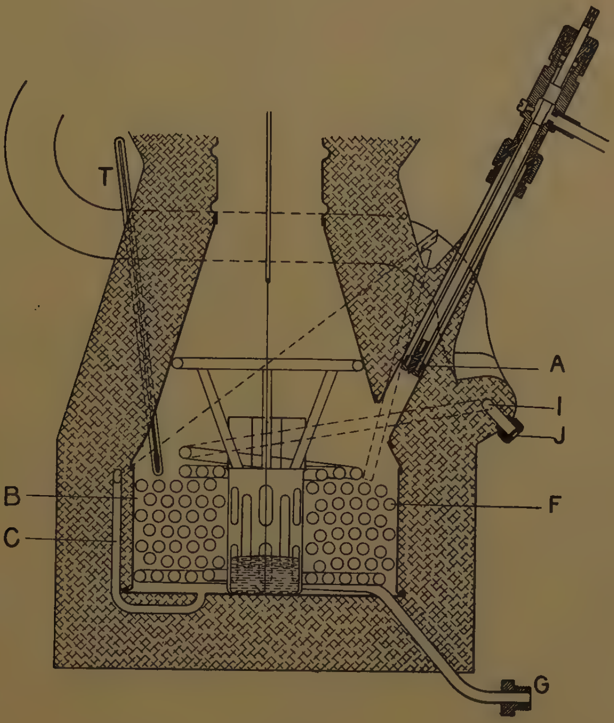

Fig. 1.

T is an alcohol thermometer, the reservoir of which is placed in a copper tube filled with alcohol, which tube is submerged into the boiling methyl-chloride.

The ethylene boiling flask (fig. 2).

The only description (with drawing) of this apparatus was given by MATHIAS in the article already quoted. It represents the old pattern. A new model was designed and constructed in 1909; since then it has been used without any alteration.

It shows a great resemblance to the methyl-chloride boiling flask. *A* is the entrance for the liquid C_2H_4; this boils (in a fairly shallow layer) in the lowest part of the chamber and the vapour rises along the spirals (wound round a central cylinder) to the escape *C*. The boiling takes place under greatly reduced pressure (± 2 cm). The compressed oxygen enters the boiling flask by *D*, and passes through a triple spiral (internal 3.5 mm, external 4.7 mm). The three parallel spirals unite into a single spiral *B* (internal 9 mm, external 11 mm), which is supported by a copper frame and end at the bottom of the flask in a few coils *F*, which are completely immersed in the boiling ethylene. The liquefied oxygen leaves the flask through the outlet tube at the bottom.

M leads to a safety valve.

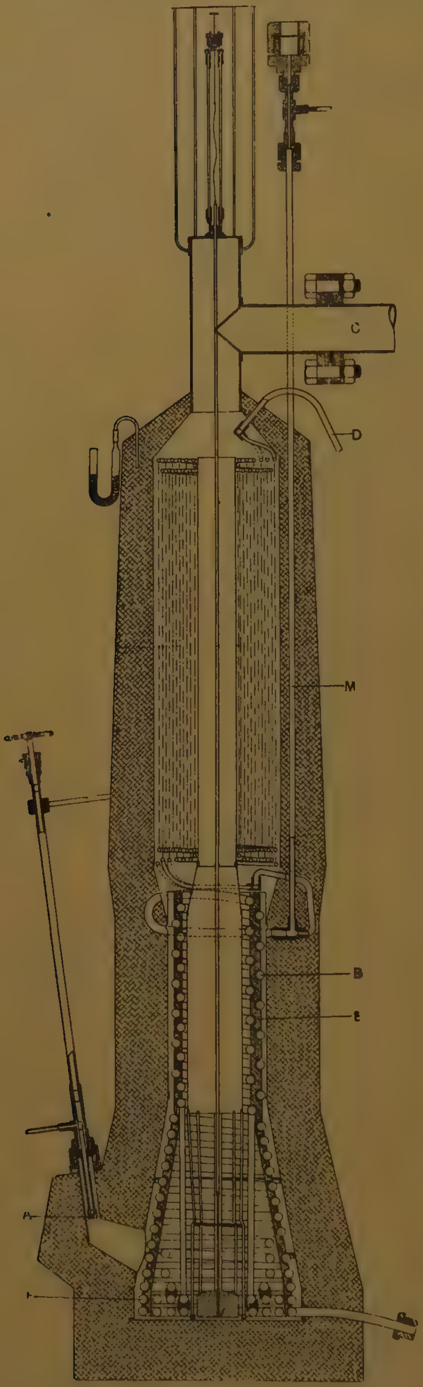

Fig. 2.

§ 2. *The hydrogen liquefier and circulation.* [1]

The hydrogen liquefier.

In Comm. N°. 94*f* a liquefier was described (X, § 2) which was constructed in the spring of 1906 and used for many years after that. In this Communication it was already said that this liquefier was only a simplified form of a more efficient model that was already designed in 1906, but had not been constructed. A schematic drawing of this better model was given in the same Comm. (pl. I. fig. 1).

An improved liquefier according to the principles on which the schematic drawing was based, was constructed and taken into use in 1912. It is being used up to the present. This apparatus raised the capacity from 4 l to 13 l liquid hydrogen per hour; the capacity of the pumps had of course to be increased.

We here give a brief description of this new liquefier. We do not need to enter into such detail as is given in the Comm. referred to; the material used and the construction of the expansion tap, of the admission tap for the liquid air, of the syphon taps for the liquid hydrogen, of the safety arrangements, of the isolation, of the floats for air and hydrogen etc. are all exactly the same as in the old model so that it is not necessary to repeat the description. The construction of the whole and in particular the arrangement of the regenerator spirals is, however, different, as can be clearly seen in the drawing (fig. 3), which represents the new liquefier in section.

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[1] See also "Gedenkboek 1922" for a description and preliminary drawings of the hydrogen and helium circulations.

The hydrogen compressed to between 150 and 200 atm. enters at the top of the apparatus and divides at once into two tubes; one leads to a spiral *B* which, as can be clearly seen in the drawing, consists of three parallel spirally wound tubes (each 6 m long)[1]), the other to a quadruple spiral *B'* (also 6 m long). These two spirals join together again and the gas then passes through the windings *C* (quadruple spiral), *D* (triple)[2]), *E* (single) and *F* (quadruple), till it reaches the tap *K*. *S* and *S'* are syphon taps by which the liquid hydrogen can be led off into vacuum vessels, to be taken to the rooms where the cryostats are built up.

Spiral *E* is completely immersed in liquid air, which is let in by the tap *L*. The drawing shows clearly, how the hydrogen is further successively cooled, when a stationary condition has been arrived at. The spirals *B'*, *C* and *F* are cooled in hydrogen vapour, *B*, *D* and *E* in air vapour and liquid air respectively.

The liquid air boils under a pressure of about 2 mm, being drawn in by a quick running horizontal vacuum pump (capacity 360 m^3 per hour).

The safety valve *M* is a small glass instrument, made so that no mercury can escape when gas bubbles pass through the mercury.

The hydrogen circulation.

A description of the hydrogen circulation, as it could be put into action in the spring of 1906, was given in Comm. No. 94f (X, § 3).

In the course of time many improvements were made in the original apparatus; the capacity of the installation in particular was increased no less than threefold by the acquisition of new compressors and the construction of a new liquefier.

The gaseous hydrogen is now first compressed to 150—200 atm. by a series of 4 compressors. These compressors, delivered by the firm of BURCKHARDT of Bâle are slow horizontal pressure pumps (about 100 revolutions per minute), which bring the hydrogen to the pressure desired by five stages. The first pump, with a volume capacity of 40 m^3 per hour, compresses 40 m^3 gas [3]) per hour from 1 to 2 atm.; the second (vol. cap. 20 m^3 per hour) works with two stages, one from 2 to 6.5 and one from 6.5 to 25 atm.; the third and fourth pump (vol. cap. 0.9 m^3 per hour) are connected in parallel and thus each deals with half of the gas introduced; they also compress in two stages, from 25 to 50 and finally from 50 to 250 atm.

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[1]) These tubes, as well as those of the other spirals, are copper tubes of 2.4 mm inner and 3.8 mm outer diameter.

[2]) The drawing is defective at the bottom of tube *C*, which there appears to be quintuple, and at the bottom of tube *D*, which seems to be there quadruple.

[3]) It is intended to acquire another new pump, which will be able to work 80 m^3, which would yield a total of 30 l liquid hydrogen per hour.

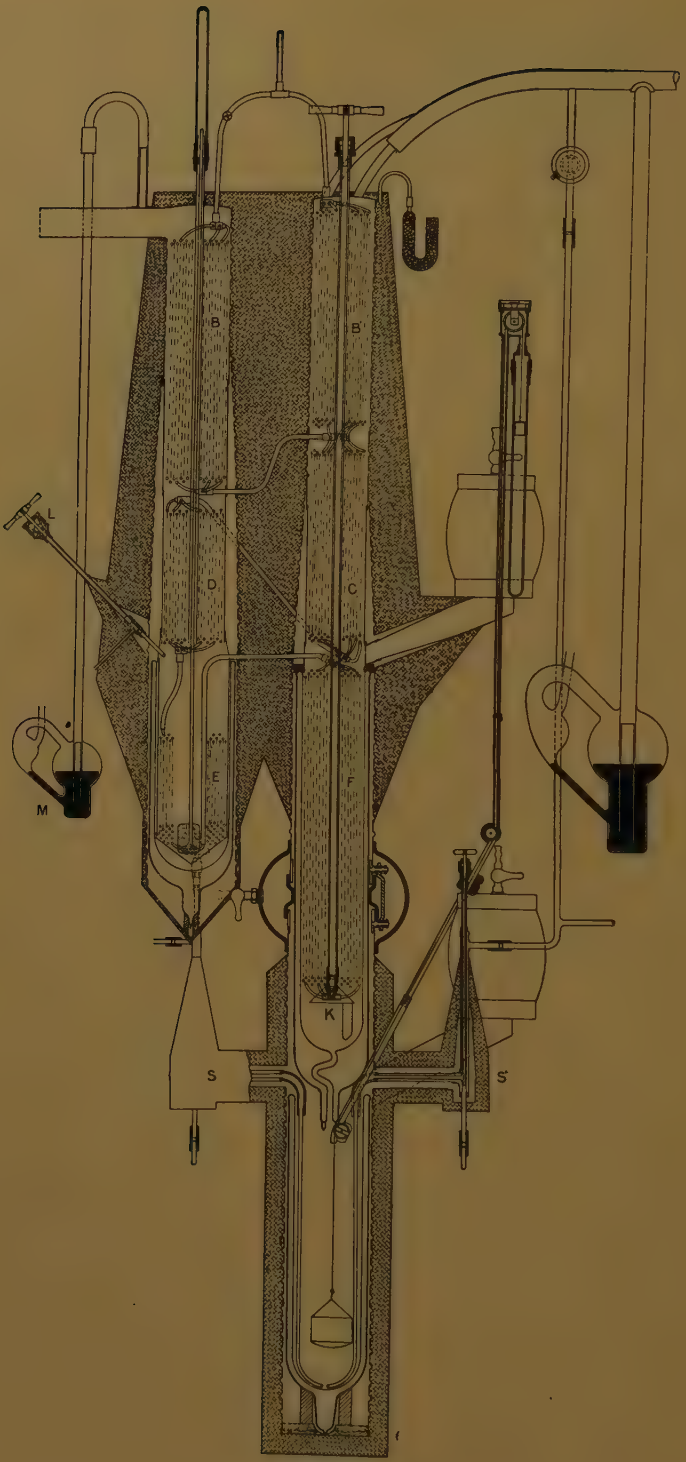

Fig. 3.

if necessary, but usually a final pressure of 150 to 200 atm. is used. Between the different stages the hydrogen is of course cooled by water.

§ 3. *The helium liquefier and circulation.*

The helium liquefier.

Up to December 1912 an old installation was used which has been described in Comm. N⁰. 108. In the old installation the preliminary time, that is the time between the beginning of the expansion and the appearance of the first drops of liquid helium, lasted an hour and the installation, when it was once going, gave 0.28 l liquid helium per hour. In 1912, 2 small compressors (of which the one could also be used as a vacuum pump) with a capacity of 5 m^3 per hour were purchased from the firm of BURCKHARDT in Bâle, which, when they were put into use considerably reduced the preliminary period, bringing it down to $^1/_2$ hour; the capacity of the liquefier was also increased, namely to $^1/_2$ l per hour. When moreover, in 1919 a new liquefier was brought into use, the circulation could be made with more than double the speed, 12 m^3 per hour; the combination of the two compressors made this result possible; the preliminary time was reduced to 20 minutes and the capacity of the liquefier was raised to 1.7 l liquid helium per hour, while moreover the use of liquid hydrogen was reduced by half.

Fig. 4 shows the new liquefier in section.[1])

The gas compressed to about 30 atm. enters at *A* and is divided into two spirals *B* and *B'*, of which the first is double and the second triple; then the two streams of gas unite again and pass through the tube *L*, which is cooled at least at the beginning in liquid air and serves as a trap to catch oil or vapour, that is to say, easily condensed impurities. After this the gas returns to regenerating spirals and is divided between the tubes *M* and *M'* (the first double, the second triple); these spirals are placed immediately beneath *B* and *B'*.

The extremities of *M* and *M'* unite again and the gas now goes to a separator *O*, consisting of a *U*-formed arrangement of two metal tubes, which contain charcoal which has been heated to redness and are immersed in liquid air; this separator serves principally to remove the last traces of air and also traces of other very volatile substances. In stationary working of the liquefier, the gas is here previously cooled to the temperature of liquid air. Now the current of gas is again divided and the gas passes once more into two spirals, the double spiral *C* and the triple spiral *C'*. These spirals are placed in a peculiar way with regard to each other, namely so that *C'* occupies the central space of a cylindrical chamber and *C* the periphery; they are separated from each other by a metal wall. The object of this construction will presently be evident. The extremities of *C* and *C'* unite once more and the gas enters the double spiral *D*, which is surrounded by vapour of liquid hydrogen, and further into the double spiral *E*, which is cooled in liquid

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[1]) The apparatus is represented in one plane; in reality the various parts are arranged in space round the central portion, that is round the actual liquefier.

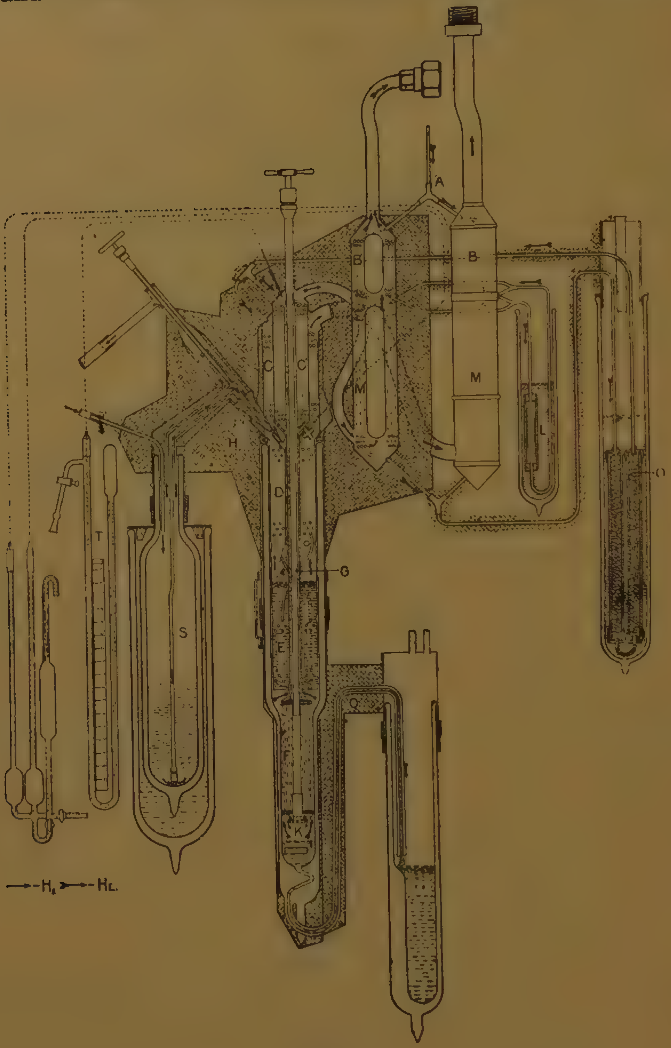

Fig. 4.

hydrogen. Here the gas is thus brought to the temperature of liquid hydrogen. The last spiral *F* is quadruple and terminates in the expansion tap *K*.

The liquid formed by expansion is collected in the space below *K* and from there it can be syphoned through the doubly bent vacuum tube *Q* into the cryostat.

The helium that is not condensed to liquid and the vapour rising from the liquid pass over the spiral *F*, which they cool; they then pass through a tube *G*, which embraces the wooden stem of the expansion tap rather closely and goes up along the axis of the hydrogen reservoir; after that this cold gas passes along the spirals *C'*, *M'* and *B'* to return finally to the compressor. The hydrogen vapour that comes out of the hydrogen reservoir, in which spiral E is placed, is used to cool successively spirals D, C, M, and B and then returns to the hydrogen compressor.

S is a reservoir of liquid hydrogen, which is itself filled from vessels of liquid hydrogen and from which the liquid in which E is immersed can be syphoned out by the tap H. The stem of this tap is cooled by the hydrogen vapour from S which vapour is then caught in the hydrogen gas container.

The liquid coming from S flows into the reservoir E through a second ring-shaped tube round the stem of K.

A few more details. The lengths of the tubes B, B', M, M', C, C', D, E and F are 2, 2, 4, 4, 2.7, 2.6, 2.5, 1.7 and 6 m respectively. The first six are again copper tubes of 2.4 mm inner and 3.8 mm outer diameter; D and E are 3.6 mm inner and 5.8 mm outer, F is 1.2 mm inner and 2.4 mm outer. The spirals B, B', M, M', have glass tubes as cores.

The height of the hydrogen surface in the reservoir round E is observed by means of a helium differential-thermometer one reservoir of which is placed at the lower end of E and the other at the lower end of D (the reservoirs are shown in the drawing). These reservoirs are connected by steel capillaries to the other parts of the thermometer, shown on the left of fig. 4.

This arrangement is simpler and easier than the thermo-needle formerly used.

There is also a thermometer reservoir with helium under the tap K. The capillary of this is connected with the thermometer T; this serves to follow the course of the regeneration process.

At the bottom of S there is a filter of metal gauze, which serves to hold back crystals of solid air and thus to prevent the hydrogen at E from being contaminated.

The vacuum glass in which the liquid helium is collected is only surrounded by a vessel containing liquid air; there is not room enough to place another vessel in between with liquid hydrogen; but it appeared that this was not necessary.

The helium circulation.

The most important particulars concerning the present circulation apparatus is found at the beginning of this §. It may be added that the large compressor has only a capacity of 5 m^3 per hour, while the liquefier needs 15 m^3 per hour. For this reason the small compressor is used as well as a forepump; it begins by compressing the gas to 2.5 atm.

For those who know the Leyden cryogenic laboratory it hardly needs saying (for those who do not know it intimately it may be said here) that the designs for the apparatus and circulations here described were made by the late Prof. KAMERLINGH ONNES in close co-operation with Mr. G. J. FLIM, technical chief of the cryogenic laboratory. The construction of the apparatus was done entirely by Mr. FLIM or under his supervision; some of the designs even are entirely his work.

Physics. — "*The melting-curve of hydrogen to* 55 *KG./cm^2.*" Communication N^0. 184*a* from the Physical Laboratory at Leyden. By H. KAMERLINGH ONNES † and W. VAN GULIK. (Communicated by Prof. W. H. KEESOM.)

(Communicated at the meeting of September 25, 1926).

§ 1. Knowledge of the course of the melting curve is of great importance, particularly in connection with the question of whether a continual change from the crystalline state of a substance into the amorphous state is possible ¹). The first question that arises then is, whether the melting curve of hydrogen continues beyond the critical temperature liquid-gas, as in the case of CO_2 ²) and PH_4Cl ³).

In order to estimate the pressure necessary for raising the melting point so far, and to test the method, we have made some determinations of the melting curve of hydrogen, to ± 55 KG./cm^2.

§ 2. *Method.* We have used the method, which is usual for the determination of the viscosity of liquids and gases by streaming in a narrow tube.

In two vessels, connected by such a tube, an imposed pressure difference will not adjust itself when a part of the tube is blocked by a plug, fixed to the wall. This can be determined with the aid of a differential manometer, the limbs of which are connected with the two vessels. Also when the pressure is greatly increased the melting point can thus be determined.

It is also a great advantage, that by a proper choice of the dimensions, the viscosity can be derived from the rapidity with which the pressure difference adjusts itself.

Two compression vessels *A* and *B* (Fig. 1), placed in a water bath, were connected by means of copper leads to the German silver tubes *C* and *D* which protruded from the cryostat, and which at their other ends were connected to the ends of a steel capillary *E* about 35 cm in length (inner diam. 0.6 mm). Metal manometer *M* shows the pressure in the steel capillary, *K* is the differential manometer. A stirrer was introduced into the cryostat and also two resistance thermometers in overlapping shunts for determining the temperature of the capillary.

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¹) Comm. Suppl. 23, § 73. See also P. W. BRIDGMAN, Change of phase under pressure. Phys. Review (2) **3**, 126, 153, 1914.

²) P. W. BRIDGMAN. Phys. Review (2) **3**, 160, 1914.

³) G. TAMMANN. Kristallisieren und Schmelzen, Leipzig 1903 p. 284—294.

After evacuation of the compression vessels and tubes, which were heated where possible, and after washing with hydrogen, supplied from tube *H*, the apparatus was filled to ± 55 KG./cm². During this operation the cock *F* was open, in order to prevent the mercury of the differential manometer going over. The equilibrium pressure at a definite temperature, which temperature is kept constant as far as possible with the aid of the resistance thermometers, was now determined as follows. We assume the temperature to be such, that the capillary is already blocked at the pressure mentioned. This is evident because, when the cock *F* is shut, and hydrogen is slowly admitted from *H* through cock *G* the differential manometer rises. Then, by opening cock *F* the difference in pressure is adjusted, and by blowing off through cock *J*, cock *F* open, the pressure is decreased until, on admitting hydrogen, cock *F* shut, the differential manometer does not rise, and so the hydrogen in the capillary is melted. The experiment is then carried out slowly in the opposite direction, till the rising of the differential manometer shows, that the hydrogen in the capillary has become solid. The pressure, which the metal manometer shows then, will be somewhat higher then the equilibrium pressure. When now, by opening and shutting *F* the pressure difference is removed and after that, hydrogen is blown off till the pressure difference, so formed, again disappears a pressure is obtained, which will be about as much lower. Thus it appeared, taking into account the temperature oscillations of the bath, that the observed pressures at which the capillary was just blocked, and at which flowing could first take place usually differed by less than 0.7 KG/cm². The manometer corrections were determined by comparison with the open

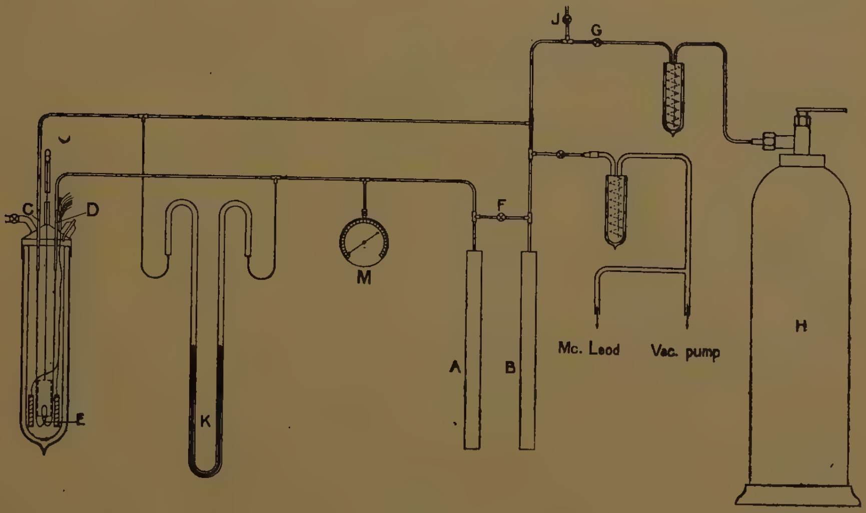

Fig. 1.

manometer to 25 KG/cm^2, and with the manometer M_{60} for the higher pressures.

§ 3. *Results.* Six points were determined in the following order:

$T_{He}Pt\ 32$	$T_{He}Pt\ 36$	T	p (KG./cm^2)	p (atm.)
15.607	15.581	$15^{\circ}.63$ K.	55.3	53.5
15.349	15.324	15.38	46.4	44.9
15.131	15.107	15.16	39.0	37.7
15.674	14.664	14.71	24.2	23.4
14.368	14.363	14.40	14.7	14.2
14.068	14.085	14.11	5.4	5.2

In Fig. 2 the melting curve is represented.

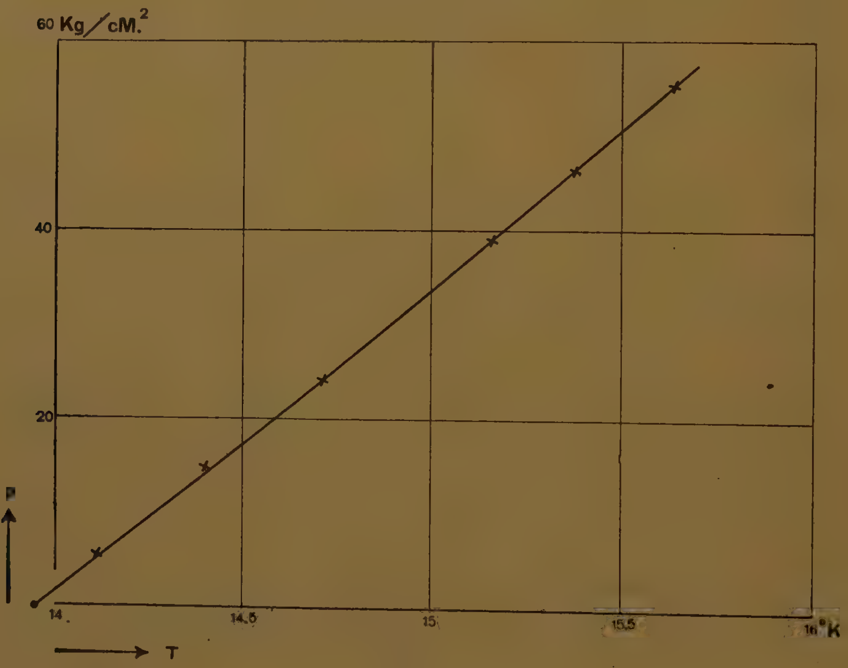

Fig. 2.

In columns 1, 2 and 4 are given means of temperature and pressure measurements (corrected) done just before and just after, or during the blocking of the capillary.

The triple point $p = 0.07$ KG/cm^2, $T = 13^{\circ}.95$ K. (Comm. N$^{\circ}$. 137*d*) forms with the points found here a sufficiently accurate continuous curve. From the values obtained follows $\left(\frac{dp}{dT}\right)_{coex.} = 33$ [1]. As the melting curve is almost straight, one obtains assuming that such an extrapolation is allowed, as a provisional estimation, for the melting pressure, corresponding with the critical temperature liquid-gas 600 KG/cm^2.

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[1] From the data of Comm. Nos. 137*a* and 153*a* for the specific volumina and the melting heat follows $\left(\frac{dp}{dT}\right)_{coex} = 77.8$. The bad agreement is perhaps owing to the fact that the determination of the density of solid hydrogen has given too small a value, probably because the solid hydrogen in the dilatometer could not contract freely because of the adhesion to the wall and so was still in a state of tension.

Physics. — *"Preliminary measurements of the dielectric constants of liquid and solid nitrogen."* By L. EBERT and W. H. KEESOM. (Communication N⁰. 182*d* from the Physical Laboratory at Leyden).

(Communicated at the meeting of September 25, 1926).

§ 1. The dielectric constants of liquid and solid nitrogen have not previously been measured. In this communication some preliminary measurements will be published. The departure of one of us is the motive for communicating these measurements, which cannot yet be considered as definite.

§ 2. *Apparatus and corrections.* The apparatus used was the same as that used for the measurements on liquid oxygen by WERNER and KEESOM[1]). We always used condenser *B* (l.c. § 2). Since the existence region of liquid nitrogen is situated wholly within that of liquid oxygen, for measurements on liquid nitrogen the cryostat could always be filled with liquid oxygen. On one occasion we succeeded in obtaining solid nitrogen in the condenser, and in taking measurements on it.

The temperature exchange took place each time with satisfactory rapidity.

The accuracy in these measurements is not so great as in those with liquid oxygen (l.c. § 5), chiefly for the following two reasons.

In the first place we did not succeed in establishing that, after a series of measurements (this is after the apparatus had been cooled to —200° C. for 24 hours or longer) the capacity of the condenser empty returned to the same value, which it had at the beginning of the measurements. As an example, in table I, two measurements are given, which are done with particular care, in order to investigate whether the geometric capacity is reproducible. Probably this effect is due to a thermic deformation, adjusting itself very slowly. Now it is difficult to establish, which zero-value of the capacity must be taken into account for each moment of a series of measurements. This uncertainty of the zero-value (5 à 7 $^0/_{00}$) surpasses that of each capacity measurement by one order of magnitude.

In the second place it is not easy to see, how large the correction for the capacity of the leading wires must be chosen in each single case. The principal thing here is the condenser consisting of the wire *D* and the metal tube *H*. The question whether the tube *H* is totally

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[1]) These Proceedings **29**, 306, 1926; Comm. Leyden N⁰. 178c.

TABLE I.

Geometric capacity of the condenser before and after a series of measurements [1]).

Date	Time	Temperature	Capacity in arbitrary units [2])
Jan. 18.26	11h a.m.	— 183° C.	32.76 ± 0.01
„ 19.26	3h p.m.	— 183	32.95 ± 0.01
May 6.26	10h a.m.	— 195	30.70 ± 0.008
„ 7.26	10h p.m.	— 195	30.97 ± 0.003

filled with the liquid to be investigated or not is then of great importance. In the first case the correction to ε is very small ($< 1\ ^0/_{00}$), in the second case it rises above $1\ ^0/_0$. The condenser was filled with nitrogen by condensation of the gas under 1 atm. overpressure, the pressure of the oxygen in the cryostat being sufficiently reduced. Filling of the cryostat with nitrogen was always continued for a long time after the liquid surface had disappeared behind the lower rim of the cap C, but for these measurements it was not possible to say to what height in H the liquid stood in each single case. Particular attention must be paid to the fact that the contraction of liquid nitrogen between boiling point and melting point amounts to $8\ ^0/_0$, so that the level of the surface in the upper, relatively narrow part of the apparatus may have fallen greatly during the course of a series of measurements. In what follows calculations were always made as if H was quite full. The correction for this not being so would *increase* the value of ε.

The temperature of the condenser was measured with the aid of the platinum thermometer T (l. c. fig. 1).

The nitrogen was taken from a cylinder, the contents of which appeared to contain according to an analysis about $3\ ^0/_{00}$ oxygen. Before the condensation the nitrogen was led through a moisture trap which was cooled with liquid air.

That the nitrogen was indeed very pure follows also from the value, which was derived from the point of retardation in the cooling curve for the freezing point, namely 63.14° K. ± 0.1°, while EUCKEN [3]) obtained for it 63.19, KEESOM and KAMERLINGH ONNES [4]) 63.06, CATH [5]) 63.23.

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[1]) Each time at the same temperature, etc.

[2]) For each number the probable error is indicated of the average derived from 5 to 10 readings.

[3]) A. EUCKEN, Verh. d. D. physik. Ges. **18**, 4, 1916.

[4]) These Proceedings **18**, 1247, 1916; Comm. Leyden N⁰. 149*a*.

[5]) These Proceedings **21**, 656, 1918; Comm. Leyden N⁰. 152*d*.

§ 3. *The results.* During the preparations for the measurements several unexpected disturbances appeared, which took considerable time to overcome. Owing to this the number of measurements, which can be considered as trustworthy, is small. Table II gives the results of these measurements.

TABLE II.

Dielectric constant of liquid nitrogen.

Date	Temperature T (°K.)	Capacity		D. C.		Density ρ	Molec. polarisation	
		C_0	C	ε_1	ε_2		P_1	P_2
Jan. 18.26	90.0	32.76	—	—	—	—	—	—
	66.7	—	47.95	1.464	(1.453)	0.8540	4.389	(4.305)
	63.9	—	48.21	1.472	(1.461)	0.8653	4.398	(4.310)
„ 19.26	76.5_4	—	47.51	(1.451)	1.440	0.8108	(4.446)	4.351
	90.0	32.95	—	—	—	—	—	—
May 6.26	78.0	30.70	—	—	—	—	—	—
	74.8	—	44.52	1.451	1.438	0.8185	4.471	4.358
„ 7.26	78.0	30.97	—	—	—	—	—	—

Regarding the separate columns of this table, the following remarks may be made.

In the two series of measurements C_0 is different owing to a thorough cleaning of the interior of the condenser and to several small repairs, which took place meanwhile.

ϱ has been interpolated from the measurements of Mathias, Kamerlingh Onnes and Crommelin 1); P indicates the expression $\frac{\varepsilon-1}{\varepsilon+2} \cdot \frac{M}{\varrho}$.

The columns ε_1, P_1 contain the values, calculated with the zero capacity *before*, ε_2, P_2 those, calculated with the zero capacity *after* the experiment.

If one of the two numbers stands between ( ), then there is a large time-interval between the measurement and the zero capacity used, in this case probably the value not placed between ( ) is preferable.

On Jan. 18, it was possible sufficiently to regulate the temperature of the cryostat for oxygen pressures of 7.6 and 5 mm respectively. So we could obtain some very preliminary values for solid nitrogen; see table III.

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1) These Proceedings **17**, 953, 1914; Comm. Leyden N⁰. 145c.

TABLE III.

Dielectric constant of solid nitrogen.				
Date	Temperature	Capacity	ε_1	ε_2
Jan. 18.26	61.9° K.	48.12	1.469	1.458
	59.9	47.90	1.462	1.452

Here we do not know ϱ, so P cannot be calculated.

§ 4. *Discussion.* a. Liquid nitrogen.

The mean of the values P not placed between ( ) from table II is 4.39. For comparison the following values can serve.

1. $\frac{n^2-1}{n^2+2} \cdot \frac{M}{\varrho}$ for liquid nitrogen at $T=77.1^\circ$ K. From data of GEROLD [1]) follows by extrapolation for $\lambda=\infty$: $n=1.1983$; ϱ is 0.8082 (see above). Then

$$R_{liq}=\frac{n^2-1}{n^2+2} \cdot \frac{M}{\varrho}=4.396.$$

2. The same expression for gaseous nitrogen at 77.97° K. and 752.3 mm. pressure. From the data of GEROLD (l.c. p. 88) follows $\varrho=0.004556$ (recalculated after BOYLE-GAY-LUSSAC). For n_∞ 1.001073 was chosen. Then

$$R_{gas}=4.395.$$

3. The same expression for gaseous oxygen under normal circumstances gives n_∞ being 1.000295:

$$R_{gas}=4.404.$$

4. The expression $P_{gas}=\frac{\varepsilon-1}{\varepsilon+2} \cdot \frac{M}{\varrho}$ for gaseous nitrogen under normal circumstances is not quite certain as the values given by various investigators are somewhat different. Recent, very careful measurements of ZAHN [2]) gave $\varepsilon=1.000581$, the lowest value, obtained till now. From this follows:

$$P_{gas}=4.34.$$

One can draw the conclusion, that the relation of MAXWELL as well as the equation of CLAUSIUS-MOSOTTI are approximately valid for gaseous and liquid nitrogen [1]). Our measurements give no data regarding the question whether it is necessary to change the formula of CLAUSIUS-MOSOTTI into the more universal formula $\frac{\varepsilon-1}{\varepsilon+u}\cdot\frac{M}{\varrho}$ (as WIENER [2]) pleads), as this question is only to be answered by means of very accurate measurements. That the number ("form number") u should differ much from 2, seems however not probable because of the approximate validity of the equation of CLAUSIUS-MOSOTTI.

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[1]) E. GEROLD, Ann. d. Phys. (4) 65, 93, 1921.

[2]) CH. TH. ZAHN, Phys. Rev. 24, 400, 1924.

Further it should be remembered, that the validity of the rule of MAXWELL speaks against the existence of an appreciable dipole-moment and of an absorption, situated in the near infra-red.

b. Solid nitrogen.

In this case the meaning of the numbers is much less clear, because the density is not known. The values of ε are smaller than the values which would be valid for liquid nitrogen at the same temperatures. It is very possible, that this only appears to be so, and that those small values are only the result of the appearance of hollows in the solid dielectricum or of the crystals being more or less directed, by which an anisotropic dielectricum may be formed. These question could only be answered by a special investigation. If the values, obtained for solid nitrogen were valid for complete and isotropic filling, then the relation of CLAUSIUS-MOSOTTI could only hold for the change liquid → solid, if the density of solid nitrogen were smaller than that of liquid nitrogen.

One of us (E.) wishes also to express his thanks to the International Education Board, for granting a stipendium, which made a sojourn in the Physical Laboratory at Leyden possible for him.

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[1]) Be it remarked that the measurements of ZAHN for oxygen under normal circumstances give for $\frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{M}{\rho}$ the value 0.1209 (see however the values of FRITS, Comm. Leyden N⁰. 178c, p. 33, note 1). This value agrees practically with the value 0.1211, which WERNER and KEESOM have obtained for the greater part of the existence region of liquid oxygen.

[2]) O. WIENER, Ber. d. Math. Phys. Kl. d. Kgl. Sächs. Ges. d. Wiss. **62**, 256, 1910; Abh. d. Math. phys. Kl. etc. **32**, N⁰. 6, 509, 1912; E. GEROLD, l.c., p. 94.

Chemistry. — *"The Cristalstructure of Gallium"*. By Prof. F. M. JAEGER, P. TERPSTRA and H. G. K. WESTENBRINK.

(Communicated at the meeting of September 25, 1926).

§ 1. In this paper the results of the structure-determinations are published, which by means of the ROENTGEN-spectrographic method were obtained in studying the pure crystallized *gallium*-metal. The *gallium* used in these investigations was prepared in a spectroscopically pure condition from a residue, which was obtained in 1915 at the *Bartlesville Zinc-Company* in *Oklahama* as an exsudation-product of the *zinc-lead*-plates ready for refining. This residu is left in the repeated distillation of the impure *zinc*: 12000 kilograms of raw material yield about 60 kilograms of the *lead*-containing residue, which do not contain more than a few grammes of *gallium* [1]. The final mixture contains, moreover, less than 8 % *indium*, less than 1 % *zinc* and only traces of *copper* and *cadmium* [2]. It was solved in pure hydrochloric acid, then potassiumhydroxide added until almost neutral reaction, and the boiling solution treated with freshly precipitated copper-hydroxide, prepared from the sixfold weight of coppersulphate by means of the necessary quantity of KOH. When all hydroxide is solved and a white, gelatinous precipitate is settled, the liquor is filtered and repeatedly treated in the same way, until no precipitate any longer appears to be formed. The collected gelatinous residue is now thoroughly washed, then solved by hydrochloric acid and the copper still present in the solution eliminated by means of hydrogensulphide. After expelling the excess of hydrogensulphide, the solution is boiled with an excess of KOH, with the purpose to eliminate *indium* and traces of *iron* eventually present: both metals will then be precipitated, while the *gallium* remains in the solution and may be separated from the filtered liquor by means of carbonic acid [3]. The precipitate thus obtained is thoroughly washed, converted on the waterbath by means of a slight excess of pure, strong sulphuric acid into *gallium-sulphate* ($+ 16\ H_2O$), and then the calculated quantity of ammonium-sulphate is added. After evaporation of the solvent into a small volume, the solution is precipitated by means of its fivefold volume of 98 %-

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[1] W. F. HILLEBRAND and J. A. SCHERRER, Journ. of Industr. and Engin. Chemistry, **8**, 225, (1916).

[2] P. E. BROWNING and H. S. UHLER, Amer. Journ. of Science, **41**, 351, (1916).

[3] All filtrates may be treated with potassiumferrocyanide and the precipitate eventually formed be decomposed by means of KOH or strong H_2SO_4 at higher temperature, to regain traces of *gallium* contained in it.

alcohol. The ammoniumgallium-alum thus prepared is solved in water, slightly acidified by some free sulphuric acid; this precipitation is repeated four or five times. The pure *gallium*-alum is solved in caustic potash, the ammonia driven out and the alkaline solution electrolyzed between platinum-electrodes. The metal thus obtained is once more converted into its hydroxide, solved in sulphuric acid, the solution, after addition of diluted sulphuric acid of 1,4 s.g., being brought to a volume of 350 ccm.; then it is electrolyzed with a current of 4 Amp. [1]). After eventually separated *indium* being eliminated, the *gallium* obtained is anodically brought to solution in diluted (1 : 10) sulphuric acid (by a current of originally 1 Amp., later of 0,1 Amp. and 12 Volt) between a wire-shaped anode and a plate-shaped cathode. The solution is evaporated till a dry residue is formed; this is solved in water and, under continuous stirring by means of a stream of gas, now electrolyzed with 4 Amp. between a plate-shaped anode and a wire-shaped cathode. *Zinc* eventually present is thus totally eliminated; the solution is again during some hours electrolyzed with 0,6 or 0,8 Amp., the consecutive fractions of separated metal are successively eliminated and after having done this about seven times, all pure *gallium* is very slowly separated from the remaining solution by means of the electric current.

The already very pure metal thus obtained is now converted into its chloride: $GaCl_3$ after the method indicated by DENNIS and BRIDGMAN [2]) and this subjected to a fractional distillation at 230°—240° C. In this way the last traces of other metals were removed, even of *zinc* and *indium*, whose chlorides boil only at much higher temperatures [3]). The pure, distilled $GaCl_3$ was then again converted into the hydroxide, this solved in caustic potash and the solution again electrolyzed between platinum-electrodes. In the spectrum of the metal thus obtained neither the *indium*-lines, nor those of *zinc* or of any other of the accessory metals originally present in the raw material, could be observed any more now. [4])

§ 2. The pure *gallium* is a beautiful, silver-white metal, melting at 30°,2 C., and once molten, remains liquid far below that temperature, it being most susceptible to undercooling-phenomena. At about 0° C. it solidifies, depending on the particular conditions of the experiment, into aggregates of larger or smaller octahedral-shaped or flattened crystals.

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[1]) LECOCQ DE BOISBAUDRAN, Ann. de Chim. et Phys., **10**, 100, (1877); H. S. UHLER and P. E. BROWNING, Amer. Journ. of Science, **42**, 389, (1916).

[2]) L. M. DENNIS and J. A. BRIDGMAN, Chem. News, **118**, 248, 256, 270, 281, 290, (1919).

[3]) The boilingpoint of $ZnCl_2$ is 730° C., that of $GaCl_3$ is 215°—220° C. $InCl_3$ is volatile at 440°, but distills very slowly only at 600° C.; about the apparatus, cf. p. 257 of the paper mentioned.

[4]) About the analytical determination of *Ga*, cf: L. E. PORTER and PH. E. BROWNING, Journ. Amer. Chem. Soc. **41**, 361, (1919); Chem. News **119**, 251, (1919).

It is very tough and cannot be powdered finely enough, so that the powder-method of HULL-DEBIJE originally seemed to promise very few results. However, it appeared possible to obtain easily somewhat larger and very good crystals of the metal, so that the crystal-structure could be investigated in details by BRAGG's spectrographic method, as well by means of rotation-spectrogramms (after SCHIEBOLD).

Crystals of *gallium* were for the first time obtained by LECOCQ DE BOISBAUDRAN ¹), the discoverer of this element. He considered them as being monoclinic, but DESCLOIZEAUX got the conviction, that they possessed tetragonal symmetry. According to WYCKOFF ²), a powder-spectrogram obtained by him, would indicate that the crystals are at least *not cubic*, as this appears to be the case with *aluminium* ³), which belongs to the same group of elements and which has a face-centred cubic grating with 4 atoms in each fundamental cell. As far as concerns the other elements of this group of the periodic system, the element *indium* would, according to SACHS ⁴), crystallize in regular octahedra; but HULL and DAVEY ⁵) demonstrated that *indium* possesses a tetragonal grating with face-centred fundamental cells, whose dimensions were found to be $a_0 = 4{,}58$ A.U. and $c_0 = 4{,}86$ A.U., the axial ratio $a : c$ therefore being: $1 : 1{,}06$; this proves that the crystals are pseudo-cubic. By means of a LAUE-spectrogram, LEVI ⁶) recently was able to prove that *thallium* possesses hexagonal symmetry.

§ 3. *The Crystalform of Gallium.*

From the molten, strongly undercooled metal rather large, very lustrous crystals of the shape reproduced in Fig. 1*a* were obtained by inoculation of the molten mass and removing the rapidly grown individuals at the right moment. If, however, the crystals are allowed to grow *slowly* from the only slightly undercooled liquid, flat, often curved crystals, which are much poorer in limiting forms are deposited, as shown in Fig. 1*b*. Afterwards we will draw attention once more to this remarkable fact, as it will appear to be intimately connected with the typical crystalstructure of this metal.

Ditetragonal-bipyramidal.

$a : c = 1 : 1{,}6753.$

Forms observed: $o = \{111\}$, predominant, very lustrous and in general

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¹) LECOCQ DE BOISBAUDRAN, Compt. rend. Paris, **83**, 1044, (1876).

²) R. W. G. WYCKOFF, The Structure of Crystals, (1924), 243. These data are until now not published.

³) Cf. the corr. literature in P. P. EWALD, *Krystalle und* RÖNTGEN*strahlen*, (1923), 292, The edge of the cubic cell would be: 4,07 A.U.

⁴) A. SACHS, Zeitschr. Kryst., **38**, 495, (1904).

⁵) A. W. HULL and W. P. DAVEY, Phys. Rev., **17**, 571, (1921).

⁶) G. R. LEVI, Nuovo Cimento, Ottobre, (1926); cf. also: Zeits. f. Kryst., **61**, 561. (1925). Although the symmetry is right, the structure indicated by this author is apparently not so, a new investigation being, therefore, necessary.

well developed; $c = \{001\}$, well developed and yielding excellent reflections; $s = \{121\}$, small, but well reflecting, mostly with only part of its faces present; $\omega = \{115\}$, extremely narrow, but measurable; $r = \{101\}$, scarcely visible, just as $\varepsilon = \{313\}$ also; the indices could, however, be determined by approximative measurements and ascertained by means of the general zone-relations. The habitus of the crystals is that of steep bipyramides, or short-prismatic according to an edge of the zone $[(001):(111)]$. The slowly developed crystals were thick tables parallel to $\{001\}$.

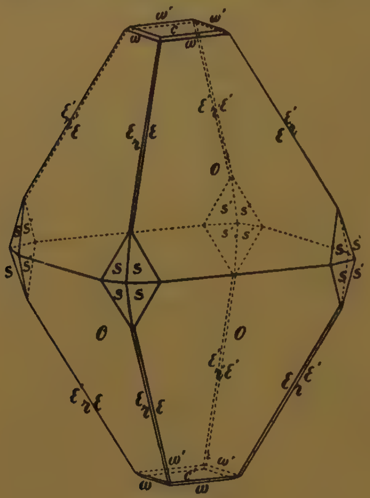

Fig. 1a.

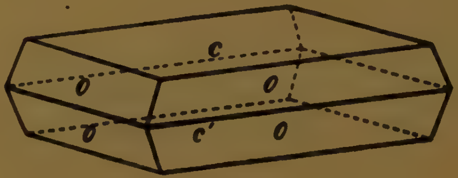

Fig. 1b.

Angular values:	Observed:		Calculated:	
$c:o = (001):(111) =$	*67	7	—	
$o:o = (111):(1\bar{1}1) =$	*81	3	81°	18′
$o:o = (111):(11\bar{1}) =$	45	35	45	46
$s:s = (121):(\bar{1}21) =$	51	6	51	12
$s:s = (121):(12\bar{1}) =$	29	30	29	$53^1/_2$
$s:s = (121):(1\bar{2}1) =$	—	—	119	34
$o:s = (111):(121) =$	19	41	19	8
$c:s = (001):(121) =$	75	7	75	$3^1/_4$
$o:r = (111):(101) =$	ca. $40^1/_2{}^\circ$		40	39
$\varepsilon:o = (313):(111) =$	ca. 24°		24	$40^2/_3$
$\varepsilon:r = (313):(101) =$	ca. 16°		15	$58^1/_3$
$c:\omega = (001):(115) =$	ca. $24^1/_2{}^\circ$		25	21
$o:\omega = (111):(115) =$	ca. $42^1/_2{}^\circ$		41	46

A stereographical projection of the forms observed is reproduced in Fig. 2.

The value of the angle $c:o$ is the mean value of five measurements and of four measurements of the angle $(111):(11\overline{1})$. The smallest value

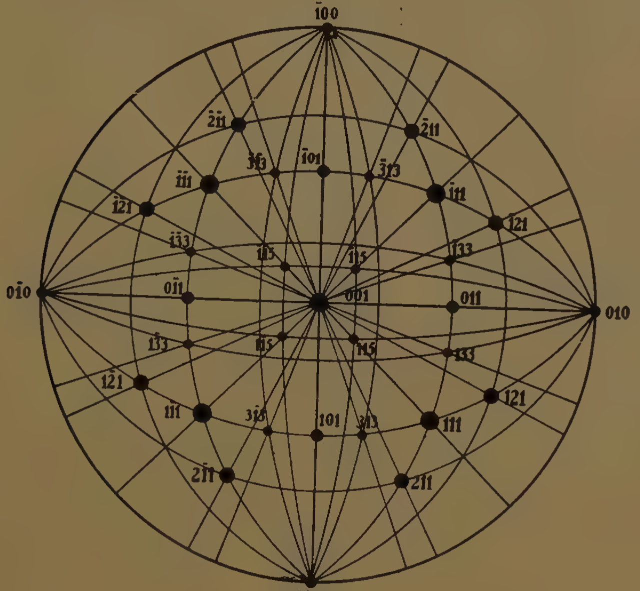

Fig. 2.

observed was 66°45′; from this last value, which differs only 22′ with the fundamental angle used in the calculation of the axial ratio, this ratio would be found to be: $a:c = 1:1{,}646$.

§ 4. In the first place spectrograms after BRAGG's method were prepared by means of the *K*-radiation of a *copper*-anticathode on a face (001) of the basis and on a face of the bipyramid {111}. At the same time the spectrum of a piece of *rocksalt* on a face of the cube {100}

TABLE I.

	$\frac{\theta}{2}$:		$\sin^2\frac{\theta}{2}$:		Spacings d in A. U.:		
	for $\lambda = Cu_\alpha$	for $\lambda = Cu_\beta$	for $\lambda = Cu_\alpha$	for $\lambda = Cu_\beta$	from: $\lambda = Cu_\alpha$	from: $\lambda = Cu_\beta$	Mean values:
Basis	11°51′	10°39½′	0.0422	0.0342	3.75	3.76	3.75^5
Bipyramid	15°13′	13°41½′	0.0689	0.0560	2.93	2.93	2.93

was photographed, with the purpose of having a spectrum for comparison, from which the true distances could be derived. The results of these measurements are given in Table I: with a distance of 60 mm between crystal and photographic plate, the accuracy of these data is about 0,02 A.U.

§ 5. Complete rotation-spectrograms were prepared with the purpose to determine 1. the identity-distances of the fundamental grating in different directions; 2. the symbols (indices and orders) of the diffracting planes in an accurate way. These spectrograms were obtained by using a modified theodolite-goniometer after GOLDSCHMIDT; this instrument is excellently adapted to this purpose, as a rotation in all desired directions may easily be effected by means of it. In most cases the crystal was moved round the axis of revolution to and fro to both sides over an angle of about 25°. In these experiments use was made of a flat photographic plate, which was suitably fixed at a distance of 40 or 50 mm. from the rotating crystal. The time of exposure was, on applying a *copper*-anticathode and a tension of about 50 K.V., ordinarily about 90 minutes.

To determine the identity-distance in the direction of the *c*-axis, a rotation-spectrogram was prepared, while the crystal was oscillating round this crystallographical axis; the distance from plate to crystal in this case was 40,5 mm. A distance of 16 mm was measured on the plate between the 1st positive and the 1st negative hyperbola; from this follows, in using the formula: $I = \frac{\lambda}{\sin \mu}$, — in which formula I is the identity-distance required, $\lambda = Cu_{\alpha} = 1{,}540$ A. U. and $\mu = arc\ tg\ \frac{8}{40{,}5}$, — that the dimension I_c in the direction of the *c*-axis is: 8,00 A.U. In connection with the data of the spectrogram after BRAGG's method, mentioned above in Table I, the conclusion must be drawn that the diffraction-image observed there is really one of the 2nd order, the spacings between the planes parallel to (001) being actually halved. The accurate value for the identity-distance I_c in the direction of the *c*-axis is, therefore, evidently: $I_c = 2 \times 3{,}75^5$ A.U. $= 7{,}51$ A.U.

A preliminary determination of the identity-distance I_a in the direction of the *a*-axis was made by means of a rotation-spectrogram, the crystal being rotated round the *a*-axis. Here the distance of the plate from the crystal was: 38,5 mm; the distance of the first positive to the first negative hyperbola on the image was: 26,5 mm, from which data the required distance I_a is calculated to be: 4,7 A.U. The final accurate determination of I_a was executed as follows.

The quadratic form for $\sin^2 \frac{\theta}{2}$ in the tetragonal system can be written as:

$$\sin^2 \frac{\theta}{2} = \frac{\lambda^2}{4a^2}(h^2 + k^2) + \frac{\lambda^2}{4c^2} l^2,$$

where *a* and *c* represent the identity-distances I_a and I_c mentioned above, in the directions considered. Now $c = I_c = 7{,}51$ A.U.; therefore $\frac{\lambda^2}{4c^2}$ has the value: 0,0105. The value for $\sin^2 \frac{\theta}{2}$ for planes parallel to (111) can be taken from Table I. If the diffraction-image after BRAGG's method is supposed to be of the 1st order, it follows from the quadratic form:

$$sin^2\,15°13' = \frac{(1{,}540)^2}{4\,a^2} \times (1+1) + 0{,}0105 \times 1;$$

or:

$$\frac{(1{,}540)^2}{4a^2} = 0{,}0292, \text{ from which is deduced: } a = I_a = 4{,}51 \text{ A. E.}$$

From the rotation-spectrogram the conclusion was already drawn, that this value for I_a needed not to be multiplied; therefore, it follows from $a = 4{,}51$ A.U. and $c = 7{,}51$ A.U., that the axial ratio $a:c$ = equal to: $1:1{,}667$ ($= \frac{5}{3}$ almost exactly). This value is in plain agreement with the results of the angular measurements of the *gallium*-crystals, by which $a:c$ was found to be: $1:1{,}6753$; for the fundamental angle $c:o$ in the latter case being: 67°7′, it would be 67°2′ for the axial ratio deduced in the above, — the difference being only 5′.

The quadratic formula for $\lambda = 1{,}540$ A.U. takes, therefore, the form:

$$sin^2\frac{\theta}{2} = 0{,}0292\,(h^2 + k^2) + 0{,}0105\,l^2,$$

and thus for the wave-length $Cu_\beta = 1{,}389$ A.U. in the same way:

$$sin^2\frac{\theta}{2} = 0{,}0238\,(h^2 + k^2) + 0{,}0086\,l^2.$$

§ 6. The dimensions of the elementary cell of the grating now being exactly known, the number N of atoms lying in each cell can be immediately computed from the formula:

$$N = \frac{V \times s}{A \times 1{,}64 \,.\, 10^{-24}},$$

in which formula V is the volume of the cell in cm³, this being $(4{,}51)^2 \times \times (7{,}51) \,.\, 10^{-24}$ cm³; s = specific weight of crystallized *gallium*[1]), this number being: 5,904 and A = atomic weight of the element, i.e. 69,9. From these numbers N is calculated as: 7,85; it must be supposed, therefore, that in each fundamental cell *eight* atoms of *gallium* must find their places.

§ 7. The other rotation-spectograms [2]), in the preparation of which the crystal was rotated round a diagonal of the upper face of the parallelopipedon or respectively round a diagonal of one of the lateral faces of the elementary cell [3]), enabled us to draw the conclusion, that the fundamental BRAVAIS' grating of the crystalstructure, must necessarily be a *simple tetragonal grating* [4]), so that neither one of the faces of it is centred, nor the centre of the cell is occupied by an atom.

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[1]) TH. W. RICHARDS and S. BOYER, Journ. Amer. Chem. Soc. 43, 274, (1921).

[2]) Cf. Tables V and VI.

[3]) These directions are resp. indicated by the zône-symbols: [110] and $[\bar{1}01]$; i.e. round the basic, resp. the polar edge of the bipyramid $\{111\}$ as axes.

[4]) This will be confirmed by the detailed study of the symbols of the diffracting planes.

a. Rotation-spectogram with revolution round the zone-axis [110].

The distance of crystal and photographic plate was: 41 mm.; the distance of the 1st hyperbola to the centre of the plate was: 10 mm., $tg\,\mu$ therefore being: $\frac{10}{41} = 0{,}2439$. From this follows: $I_{[110]} = 6{,}5$ A.U., while from the true value for I_a ($= 4{,}51$ A.U.), the diagonal of the basal face of the elementary cell is calculated to be: $4{,}51\sqrt{2}$ A.U. $= 6{,}38$ A.U., which is in good agreement with the experimental result.

b. Rotation-spectrogram with rotation round $[\bar{1}01]$ (*polar edge of* {111}).

The distance of the crystal and the plate was here: 45 mm.; the distance of the 1st hyperbola to the centre of the plate was: 17 mm.; therefore: $tg\,\mu = \frac{17}{45} = 0{,}3777$ and $I_{[\bar{1}01]} = 8{,}2$ A.U. Calculation, on the other side, shows, that the diagonal of the lateral face of the elementary cell is: $\sqrt{(4{,}51)^2 + (7{,}51)^2}$ A.U. $= 8{,}7$ A.U. Here also there is a perfect agreement between calculated and observed value.

§ 8. With the aid of the quadratic formula found in the foregoing pages, it was now further possible to make a complete analysis as well of the different rotation-spectograms, as of the powder-spectogram finally obtained in the following way. As was said already, by the specific properties of the *gallium*-crystals, which are very tough and which probably possess, moreover, gliding-faces, — it was almost impossible to grind them down into a powder of sufficiently fine grains. A thin silk thread rubbed with this powder was covered with it, but if stretched along the axis of the camera, no interference-images after HULL-DEBIJE's method could be obtained on the film. We succeeded, however, by grinding the *gallium* in a mortar under liquid air and smearing the silk thread, [1]) also under liquid air, with the finest *gallium*-dust in the mortar. *Gallium* gets very brittle at the temperature of liquid air and can be ground then easily into very fine powder; in the subsequent rising of the temperature, the original grating is preserved in the dust sticking to the silk thread, and now a real powder-spectogram could be observed, only locally marred by small black patches, showing that some grains of the powder were not yet fine enough. However, the film could readily be made use of for the estimation of the relative intensities of the diffraction-lines.

The results of the analysis of the powder-spectograms, as well of that of the different rotation-spectrograms already mentioned in § 5 are reviewed in the Tables II till VI. If necessary, besides the indices h, k and l with respect to the ordinary crystallographical axes, also the indices h', k' and l' are mentioned, which are related to axes of which one coïncides with the axis of rotation of the crystal in each case. The purpose of these last indices is to prove, that the indices *h*, *k* and *l*, as derived from the quadratic equation, are *not* contradictory to the sequence-numbers of the successive hyperbolae on the films, on which hyperbolae the corresponding interference-image is arranged. The necessary transformation-equations, by which h', k' and l' are calculated from *h*, *k* and *l*, are also given in the tables.

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[1]) It is remarkable, that the silk preserves it plasticity also at the temperature of the liquid air.

§ 9.

TABLE II.

Analysis of the Powder-spectrogramm of Gallium.

(Radius of the camera: 25 mm)

Distance $2l$ in m.m.:	Wave-length:	$\frac{\theta}{2}$:	$\sin\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$ (observed):	$\sin^2\frac{\theta}{2}$ (calculated):	Symbols $(h\,k\,l)$:
19.70	Cu_β	11°23′	0.1970	0.0387	0.0324	(002)
					0.0324	(101) *)
20.10	Cu_α	11°38′	0.2016	0.0408	0.0420	(002)
23.48	„	13°56′	0.2351	0.0554	0.0562	(111)
26.24	Cu_β	15°11′	0.2619	0.0686	0.0689	(111)
30.80	Cu_α	17°49′	0.3060	0.0936	0.0952	(200)
34.48	Cu_β	19°50′	0.3393	0.1151	0.1166	(200)
39.22	Cu_α	22°42′	0.3859	0.1490	0.1460	(210) *)
					0.1529	(113)
40.25	„	23°18′	0.3956	0.1565	0.1565	(211)
					0.1588	(202)
44.04	„	25°30′	0.4305	0.1853	0.1880	(212)
49.71	„	28°46′	0.4812	0.2316	0.2336	(220)
51.18	Cu_β	29°37′	0.4942	0.2442	0.2466	(311)
					0.2486	(302)
55.09	Cu_α	31°53′	0.5282	0.2792	0.2756	(222)
57.63	„	33°21′	0.5498	0.3023	0.3025	(311)
					0.3048	(302)

About ten weak lines, following the last mentioned one, were omitted here, as they have no significance for our purpose. The tension was here 55000 Volts; the time of exposure: 3 hours.

§ 10.

TABLE III.

Rotation-spectrogram with revolution round the *c*-axis.

(The distance from plate to crystal was: 41 mm)

Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$ (observed):	$\sin^2\frac{\theta}{2}$ (calculated):	Symbols $(h\,k\,l)$:
0	62.5	28°22′	0.2257	0.2336	(220)
1	24.0	15°10′	0.0684	0.0689	(111)
1	42.4	22°59′	0.1524	0.1565	(211)
— 1	24.0	15°10′	0.0684	0.0689	$(11\bar{1})$
2	48.6	25°19′	0.1810	0.1880	(212)
— 2	50.1	25°21′	0.1833	0.1880	$(21\bar{2})$
3	40.3	22°15′	0.1434	0.1529	(113)

§ 11.

TABLE IV.

Rotation-spectrogram with revolution round the *a*-axis.

(The distance from plate to crystal was: 40.5 mm)

Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$ (observed):	$\sin^2\frac{\theta}{2}$ (calculated):	Symbols $(h\,k\,l)$:
0	17.8	11°52′	0.0423	0.0420	(002)
0	43.8	23°37′	0.1605	0.1680	(004)
				0.1588	(022)
1	40.3	22°4′	0.1452	0.1460	(120) *)
				0.1529	(113)
1	64.0	28°50′	0.2326	0.2405	(123)
				0.2264	(114)
2	50.0	25°30′	0.1854	0.1880	(122)

§ 12.

TABLE V.

Rotation-spectrogram with the revolution round the direction [110].
(The distance from plate to crystal was: 41 mm)

Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$ (observed):	$\sin^2\frac{\theta}{2}$ (calculated):	Symbols $(h\,k\,l)$:	$(h'\,k'\,l')$ (Reduced on the axis):
0	45.5	24°0′	0.1665	0.1680	(004)	(004)
0	18.6	12°12′	0.0447	0.0420	(002)	(002)
1	53.5	26°16′	0.1959	0.1972	(104)	$(1\bar{1}4)$
1	25.5	15°56′	0.0754	0.0712	(102)	$(1\bar{1}2)$
2	42.5	23°1′	0.1529	0.1529	(113)	(203)
3	51.0	25°36′	0.1867	0.1880	(212)	$(3\bar{1}2)$

Transformation-formulae:

$$h' = h + k \;;\; k' = k - h \;;\; l' = l.$$

The index h' belongs to the axis of revolution.

§ 13.

TABLE VI.

Rotation-spectogram with the revolution round the direction $[\bar{1}01]$.
(The distance from plate to crystal was: 45 mm)

Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$ (observed):	$\sin^2\frac{\theta}{2}$ (calculated):	Symbols $(h\,k\,l)$:	$(h'\,k'\,l')$ (Reduced on the axis):
0	26.6	15°17′	0.0695	0.0689	(111)	(110)
0	39.5	20°38′	0.1242	0.1168	(020)	(020)
1	56.5	25°44′	0.1885	0.1880	(122)	(121)
—1	47.6	23°19′	0.1567	0.1565	(211)	$(21\bar{1})$
2	46.5	22°58′	0.1522	0.1529	(113)	(112)
—2	26.6	15°17′	0.0695	0.0689	$(11\bar{1})$	$(11\bar{2})$
—2	72.0	29°0′	0.2350	0.2336	(220)	$(22\bar{2})$
—3	47.7	23°20′	0.1569	0.1569	$(21\bar{1})$	$(21\bar{3})$
—3	58.5	26°13′	0.1952	0.1972	$(\bar{1}0\bar{4})$	$(\bar{1}0\bar{3})$
4	51.5	24°26′	0.1711	0.1680	(004)	(0 04)
—4	49.0	23°43′	0.1618	0.1588	$(20\bar{2})$	$(2\,0\bar{4})$

Transformation-formulae:

$$h' = h \;;\; k' = k \;;\; l' = l - h.$$

The index l' belongs to the axis of revolution.

§ 14. For the determination of the space-group the tables of ASTBURY and YARDLEY ¹) were made use of. From the spectrograms described above, it is evident, that interference-images belonging to atomic planes with the symbols of the type: $(h\,k\,0)$, in which $(h+k)$ is *odd*, and of the type: $(0\,k\,l)$, in which l is odd, were *not* observed with certainty. Such uncertain symbols were indicated by an asterisk *) in the tables. All other combinations of indices were observed; but in the case of the symbols thus indicated with an asterisk, always another combination of indices appeared to be possible also.

As *gallium*, according to the crystallographical measurements, very probably possesses ditetragonal-bipyramidal symmetry, — as becomes evident, for instance, from the fact, that some crystals, as in Fig. 1a, manifest the full number of faces of each form in perfectly well-balanced development, — the four only space-groups possible here amongst the twenty groups belonging to this crystal-class, are, in WYCKOFF's notation ²):

D^1_{4h}: no halving of spacings between atomic planes what so ever;

D^7_{4h}: halving of spacings between atomic planes of the type: $(h\,k\,0)$, in which $(h+k)$ is *odd*;

D^{10}_{4h}: halving of spacings between atomic planes of the type: $(0\,k\,l)$, in which l is *odd*;

D^{16}_{4h}: halving of spacings between atomic planes of the types: $(h\,k\,0)$, in which $(h+k)$ is *odd*, and of the type: $(0\,k\,l)$, in which l is *odd*.

To fix the choice between these, it is, therefore, of the highest importance now, to determine with full certainty the yet problematic indices of those interference-images, for which from the quadratic equation alone, hitherto no choice could be made between e.g. (101) (Cu_α) and (002) (Cu_β), or between (210) and (113); etc. The rotation-spectograms, described in the tables III till VI, were principally prepared with the purpose of determining the identity-distances in the directions of revolution: but now it appeared necessary to prepare some others, with the intention to exclude with absolute certainty those indices, which were yet doubtful; the choice between the four space-groups mentioned can only be made, if the indices-triples really present, be determined beyond any doubt.

In the way followed up till now, it was, as already said, not possible to fix the choice between some of the symbols, as calculated from the quadratic equation, because the values of $sin^2 \frac{\theta}{2}$ thus computed, did not differ sufficiently from each other. Therefore, in preparing the new rotation-spectrograms, which are reviewed in the tables VII till XI following here-after, — it was in each case necessary to determine accurately,

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¹) W. T. ASTBURY and K. YARDLEY, "Tabulated data for the Examination of the 230 Space-groups by homogeneous X-rays", Londen, (1924), Proceed. Royal Soc., A, 224, 221—257.

²) R. W. G. WYCKOFF, "The Analytical Expression of the Results of the Theory of Space-groups", Washington, (1922), Carnegie-Publ. Nº. 318.

between what extreme angular limits in both directions the rotation round the axis of revolution really took place during the experiment. It was possible, by making a stereographical projection of the scattering planes with the aid of a WULFF's plot and rotating that projection through the same limiting angles as were used in the case of the rotating crystal, — to ascertain, whether these planes had really been in such positions, as possibly to give the diffraction-images of the symbols, which were supposed to have been observed in each special case. In this way it could be verified rigorously, whether atomic planes, to which simple indices were attributed, really had been in such favourable positions for giving interference-images or not, and whether some of them were absent, although those atomic planes might have been in the right positions for scattering the incident *X*-rays.

§ 15. In the spectrogram, to which table VII refers, the crystal was rotated round the direction $[\bar{1}01]$ in such a way, that in both directions an angle of 29° was covered, starting with a position, in which the primary pencil of *X*-rays was parallel to (111). By means of the stereographical projection it could be stated, that the atomic planes mentioned in table VII, had really been in the required „reflecting" positions. As

TABLE VII.

Rotation-spectrogram with revolution round the direction $[\bar{1}01]$.
(Distance between crystal and plate: 54.5 mm)

Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$ (observed):	$\sin^2\frac{\theta}{2}$ (calculated):	Symbols $(h\,k\,l)$:	Symbols $(h'\,k'\,l')$ (reduced):
0	32.1	15°15′	0.0691	0.0689	(111)	(110)
0	45.5	19°56′	0.1162	0.1168	(020)	(020)
1	57.5	23°16′	0.1560	0.1565	$(\bar{2}1\bar{1})$	$(\bar{2}11)$
—1	33.0	15°36′	0.0723	0.0712	$(\bar{1}0\bar{2})$	$(\bar{1}0\bar{1})$
2	45.5	19°56′	0.1162	0.1168	$(\bar{2}00)$	$(\bar{2}02)$
—2	25.0	12°19′	0.0455	0.0420	$(00\bar{2})$	$(00\bar{2})$
—2	55.5	22°46′	0.1499	0.1529	$(\bar{1}1\bar{3})$	$(\bar{1}1\bar{2})$
3	58.0	23°23′	0.1575	0.1565	$(\bar{2}11)$	$(\bar{2}13)$
4	56.0	22°53′	0.1512	0.1529	$(\bar{1}13)$	$(\bar{1}14)$
—4	61.0	24°7′	0.1667	0.1680	$(00\bar{4})$	$(00\bar{4})$

Transformation-formulae:

$$h' = h \ ; \ k' = k \ ; \ l' = l - h.$$

The index l' refers to the axis of revolution.

the indices attributed to them appeared to be in full agreement with the subsequent hyperbolae on the film, as well with the quadratic equation, *their exactness is sufficiently assured in this case.*

§ 16. In the same way table VIII gives a review of the results obtained on rotating the crystal round the *c*-axis. If the position in which the primary pencil of *X*-rays is parallel to the plane (110), is called the position for which $\frac{\theta}{2} = 0°$, — then the crystal appeared in this case to be rotated from $\frac{\theta}{2} = -11°$ till $\frac{\theta}{2} = +35°$. The plane (110) should have given a diffraction-image of the 1st order for $\frac{\theta}{2} =$ circa 14°, and a 2nd order image at about $\frac{\theta}{1} = +28°$; but a 1st order image was *not* observed in this case.

TABLE VIII.
Rotation-spectogram with revolution round the *c*-axis.
(Distance between crystal and plate: 42.5 mm)

Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$ (observed):	$\sin^2\frac{\theta}{2}$ (calculated):	Symbols $(h\,k\,l)$:
0	67.0	28°48′	0.2321	0.2336	(220)
0	35.0	19°44′	0.1140	0.1168	(200)
1	25.0	15°14′	0.0691	0.0689	(111)
1	44.0	23°0′	0.1527	0.1565	(211)

§ 17. The table IX refers also to a rotation-spectrogram with revolution round the *c*-axis. But now the crystal was rotated between the

TABLE IX.
Rotation-spectrogram with revolution round the *c*-axis.
(Distance between crystal and plate: 42 mm)

Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$ (observed):	$\sin^2\frac{\theta}{2}$ (calculated):	Symbols $(h\,k\,l)$:
0	26.7	19°47′	0.1146	0.1166	(200)
0	66.3	28°50′	0.2326	0.2336	(220)
1	43.9	23°16′	0.1561	0.1565	(211)
3	43.5	23°0′	0.1527	0.1529	(113)

limits: $\frac{\theta}{2} = -15^\circ$ and $\frac{\theta}{2} = +31^\circ$, if $\frac{\theta}{2} = 0$ is now the position, in which the plane (100) is parallel to the primary beam. The atomic planes (101), (100) and (210) will now all come into positions favourable for the occurrence of interference-images of the 1st order. Notwithstanding this, however, *no* such images were observed here.

§ 18. In table X the results are collected, which refer to a rotation-spectrogram with revolution round the *a*-axis. In the mean position the primary beam was parallel to the plane (001), and from this position the rotation took place in both directions through an angle of 23°. An interference-image of the plane (013) could now be expected, but on the film no trace of it could be discovered. The other planes of {013} do not come into positions favourable for "reflection". Moreover, no interference-images of atomic planes can occur with the symbols: (102), $(10\overline{2})$, (202), $(20\overline{2})$ and neither of the planes of {210}; the indices given in table X, therefore, must be the only possible ones.

Another spectrogram of this kind was made, moreover, in which the only difference with the preceding case consisted in this, that the crystal, — having its mean position, when (001) was parallel to the primary pencil of *X*-rays, — was first turned 60° in the direction of this primary beam and then rotated from this new position over 23° to both sides of it. In this case it might namely have been possible for (210), to give a diffraction-image; but even now, this image was *not* present on the film. In this experiment the planes of {113} could not give any confusion in the decision about the presence or absence of the image from (210), because the images belonging to this form would be situated on other hyperbolae; moreover, of all its planes, only $(\overline{1}\,1\,\overline{3})$ could arrive in a "reflecting" position, and its image was really observed on the film. Also an image from (110) could be expected in this case; but it was absent once more in the spectrogram obtained.

TABLE X.

Rotation-spectrogram with revolution round the *a*-axis.
(Distance between crystal and plate: 45 mm)

Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$ (observed):	$\sin^2\frac{\theta}{2}$ (calculated):	Symbols $(h\,k\,l)$:
0	20.0	11°59′	0.0431	0.0420	(002)
1	27.0	15°29′	0.0712	0.0689	(111)
1	46.0	22°49′	0.1504	0.1529	$(\overline{11}3)$
2	48.5	23°36′	0.1603	0.1565	(211)

TABLE XI.

Rotation-spectrogram with revolution round the *a*-axis.

(Distance between crystal and plate: 46 mm)

Number of the hyperbolae:	Distance of Spots from the centre in mm:	$\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$ (observed):	$\sin^2\frac{\theta}{2}$ (calculated):	Symbols $(h\,k\,l)$:
0	39.0	20°9′	0.1187	0.1168	(020)
0	49.0	23°24′	0.1577	0.1588	(022)
1	27.0	15°18′	0.0696	0.0689	(111)
−1	47.6	23°0′	0.1527	0.1529	$(\bar{1}13)$
2	50.0	23°42′	0.1616	0.1588	(202)
				0.1565	$(21\bar{1})$

§ 19. After the analysis and study of the spectrograms reviewed in the tables VII till XI, the conclusion can be drawn with sufficient certainty, that really no other space-groups than D^1_{4h}, D^7_{4h}, D^{10}_{4h} and D^{16}_{4h} are possible in the case of the *gallium*-crystals, while all other space-groups can readily be excluded. On the other hand it becomes highly probable, that amongst those D^{16}_{4h} is the right one, because of the fact, that the interference-images corresponding with atomic planes having the symbols $\{h\,k\,0\}$ and $\{0\,k\,l\}$, in which respectively $(h+k)$ or l are *odd*, appear to have systematically an intensity equal to *zero*, at least in so far as this could be proved. However, it is advisable to investigate by means of calculating the relative intensities, whether perhaps one of the other space-groups might also be taken into account in this respect, so that the 8 atoms were arranged in such a way within each elementary cell, that a sufficient agreement between the calculated intensities and those observed in the powder-spectrogram were obtained. The powder-spectrogram is much better suited for this purpose than the rotation-spectrograms, for which an accurate calculation of the intensities is hardly possible.

The calculation of the intensities in the powder-spectrogram was effectuated by means of the well-known formula:

$$I = \frac{1+\cos^2\theta}{2\cos\frac{\theta}{2}\,.\,\sin^2\frac{\theta}{2}}\,.\,n\,.\,|S|^2,$$

in which n is the number of planes of the complete crystalform $\{h\,k\,l\}$, and $|S|$ signifies the absolute value of the structural factor, in such a way, that:

$$|S|^2 = |\Sigma\, e^{2\pi i(hm+kn+lp)}|^2 = |\Sigma \cos 2\pi(hm+kn+lp)|^2 + \Sigma\, |\sin 2\pi(hm+kn+lp)|^2$$

is [1]).

The estimated intensities of the lines of the powder-spectrogram are reviewed in the 2nd column of table XII. A practically unobservable small intensity was found to be present for lines, corresponding with (001), (100), (110), (101), (103) and (120); with exception of (110), all these symbols belong really to one of the types: $\{h\,k\,0\}$ or $\{0\,k\,l\}$, with respectively $(h+k)$, or $l =$ *odd* number.

A review of all possible combinations of 8 equivalent points compatible with these space-groups, is given in WYCKOFF's tables. (Cf: *Analytical Expression*, etc., (1922), p. 89—102).

A. Space-group D_{4h}^1.

In this case *five* combinations of 8 equivalent points are possible, which cases are discerned by the author as *p*, *q*, *r*, *s* and *t* (loco cit. p. 90).

The arrangement of the atoms according to the coordinates mentioned sub *p* is excluded, because of the fact that the spacing of the atomic planes parallel to (001) would not be halved, while experiment shows that this actually takes place. The same argumentation is valid for an arrangement of the atoms according to the coordinates mentioned sub *q*. Moreover, the combination *r*, *s* and *t* appear to be excluded, because if the parameter v in the direction of the *c*-axis be taken equal to $\frac{1}{4}$, the spacing, between the planes parallel to (001) is, indeed halved, but the identity-distance I_c appears to be shortened simultaneously to half its true value: then the cell would no longer contain 8, but only 4 atoms, what is in contradiction with experience. Therefore, the whole space-group D_{4h}^1 must be excluded.

B. Space-groups D_{4h}^7.

Here *four* cases are possible of 8 equivalent places symmetrically arranged, which by the author are discerned as the cases *g*, *h*, *i* and *j* (loco cit., p. 93). The combinations *g* and *h* are excluded according the same arguments, which in the previous case led to the exclusion of the cases *p* and *q*. The combinations mentioned sub *i* and *j* are impossible, because the intensities of (110) and (001) must be both *zero*, which only occurs if $u = v = \frac{1}{4}$. But then the intensity of (101) in case *i* would be very great, while it is *zero* in reality; in case *j* the intensities of (113) and (212) become also *zero*, which is not in accordance with experience, as may be seen from the results formerly discussed. The space-group D_{4h}^7 is, therefore, also excluded.

C. Space-group D_{4h}^{10}.

Five cases, discerned in the tables as *k*, *l*, *m*, *n* and *o*, are possible here for arrangements of 8 equivalent points in a way compatible with the special symmetry of this space-group (loco cit., p. 95).

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[1]) The question, several times already discussed in recent days, whether the intensity I may be supposed to be really proportional to $|S|^2$, or whether it be more in conformity with the actual situation, in supposing a proportionality to $|S|^n$, in which n lies between 1 and 2, — is now left out of consideration here.

The case mentioned sub *k* must be excluded, because the mutual arrangement in this case would be such, that halving of spacings would occur, if *l* be odd; for in this case the sums $(hm + kn + lp)$ differ pairwise just with an exact amount of $\frac{l}{2}$, so that in the structural factor *S* always sinus and cosinus of angles will appear combined, which differ from each other with the value π, with the result that these numbers will totally annihilate each other. For $l = odd$, all corresponding intensities, therefore, will get the value *zero*, which is contradictory to experience, because e.g. (111) and (113) are certainly observed with measurable intensity. The case *k* is thus excluded, and the same argumentation is valid for the combinations mentioned sub *l* and *m*; the cases being, therefore, also impossible here. Considering the cases *n* and *o*, it may be remarked, that the intensities of (100), (110) and (210) must be *zero*, which only takes place, if $u = v = \frac{1}{4}$. But then the intensity of (211) appears also to become *zero*, which is contradictory to the experimental results. From this follows, that both cases *n* and *o* are excluded, and therewith the whole space-group D_{4h}^{10}.

D. The space-group D_{4h}^{16}.

Within this group *four* cases of 8 equivalent positions must be discerned, which in the tables are indicated sub *f*, *g*, *h* and *i* (loco cit., p. 98). The combination mentioned sub *f* is excluded beforehand, because the coördinates corresponding to *h* and *k* are not variable here: thus, e.g. the intensity of (110) cannot get the value $= 0$, while experiment reveals this fact with certainty. The combinations of points mentioned sub *g* and *h* are equally excluded, because in these cases *p* must be taken equal to *zero* or to $\frac{1}{2}$. The sum of the sinus and that of the cosinus in the structural factor *S* must be equal to *zero*, therefore, not only for $l = 0$, but also if *l be even*, because in that case, for $p = \frac{1}{2}$, the corresponding angle is increased with a whole number, multiple of 2π. Now the intensity of (210) appears really to be *zero*, as might be expected in the space-group D_{4h}^{16}; but according to what was said above, also the intensity of (212) should be *zero* in that case, while experiment has taught the contrary.

It therefore appears, that only the case mentioned sub *i* remains possible here. The parameters of the 8 equivalent points in this case are:
$[u, (u + \frac{1}{2}), v]$; $[u, (\frac{1}{2} - u), (v + \frac{1}{2})]$; $[-u, (\frac{1}{2} - u), v]$; $[u, (u + \frac{1}{2}), (v + \frac{1}{2})]$;
$[(u + \frac{1}{2}), u, -v]$; $[(u + \frac{1}{2}), -u, (\frac{1}{2} - v)]$; $[(\frac{1}{2} - u), -u, -v]$; en $[(\frac{1}{2} - u), u, (\frac{1}{2} - v)]$.

The symmetry of this atomic arrangement is characterized by the presence of tetragonal screw-axes: $[001]_{0,1/2}$ and $]001]_{1/2,0}$; diagonal rotation-axes: $[001]_{0,0}$ and $[001]_{1/2,1/2}$; eight symmetry-centra:
$[\frac{1}{4}, \frac{1}{4}, 0]$, $[\frac{2}{4}, \frac{1}{4}, \frac{1}{2}]$, $[\frac{3}{4}, \frac{3}{4}, 0]$, $[\frac{1}{4}, \frac{3}{4}, \frac{1}{2}]$, $[\frac{1}{4}, \frac{1}{4}, \frac{1}{2}]$, $[\frac{3}{4}, \frac{1}{4}, 0]$, $[\frac{3}{4}, \frac{1}{4}, \frac{1}{2}]$ and $[\frac{1}{4}, \frac{3}{4}\, 0]$;

gliding-mirror planes $(001)_0$ and $(001)_{1/2}$, with translations in (001); idem such: $(110)_0$, $(1\bar{1}0)_0$, $(100)_0$, $(100)_{1/2}$, $(010)_0$, and $(010)_{1/2}$, with translations parallel to the *c*-axis; rotation-mirrorplanes: $(001)_{1/4}$ and $(001)_{3/4}$; and mirrorplanes: $(110)_{1/2}$ and $(1\bar{1}0)_{1/2}$.

It could be shown, that indeed a sufficient agreement between the observed and calculated intensities could be obtained (cf. table XII), if for *u* the value: $\frac{8}{40}$ or $\frac{9}{40}$, and for *v* the value $\frac{6}{40}$ or $\frac{7}{40}$ be substituted. A more accurate calculation of the parameters is impossible, while the observed, or rather: the estimated intensities are known only too inaccurately. It may be remarked, that in this case the smallest distance of two *Ga*-atoms appears to be: 2,56 A.U., while, according to W. L. BRAGG, the "atomic radius" of the *Ga*-atom should be 1,3 A.U., which is as perfect an agreement as one could desire.

Fig. 3, 4 and 5 may give an image of the structure of the elementary cell in perspective and in orthogonal projection on a face of (001); in Fig. 3 the four successive layers atoms *A*, *B*, *C* and *D* and the places of their centres are drawn and the different dimensions in the direction of the *c*-axis indicated. In each layer the atoms are arranged as indicated

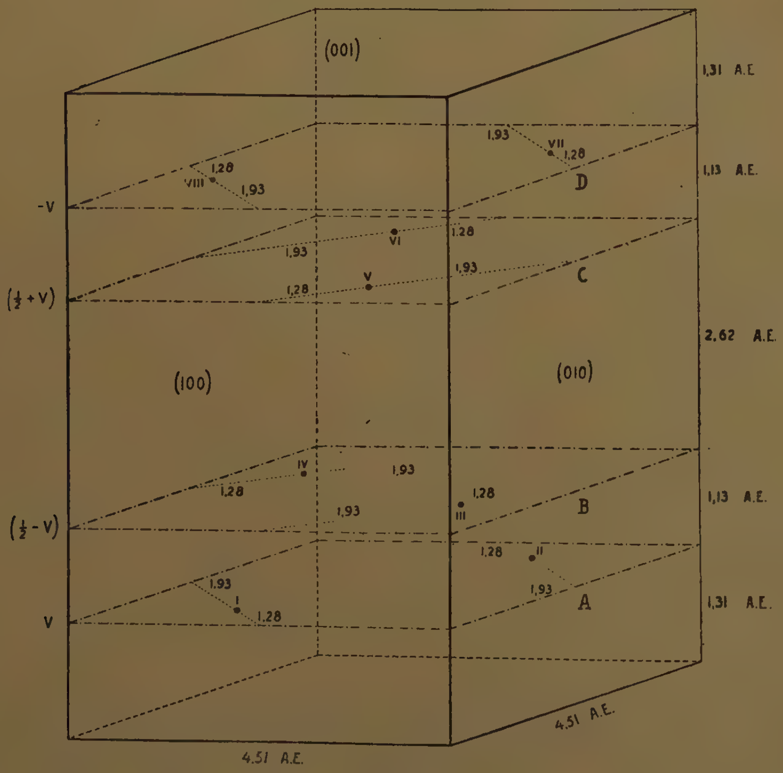

Fig. 3.

TABLE XII.

Symbols $(h\,k\,l)$:	Estimated intensities:	Calculated intensities ($\times$ 10000):			Mean calculated intensities
	$(\lambda = Cu_\alpha)$	for: $u=\frac{8}{40}$; $v=\frac{6}{40}$:	for: $u=\frac{8}{40}$; $v=\frac{7}{40}$:	for: $u=\frac{9}{40}$; $v=\frac{7}{40}$:	$\times\frac{1}{250}$:
(110)	0	30	30	0	0.08
(002)	6	300	1100	1100	3 à 4
(111) ; (102)	8	2000 + 600	1100 + 200	1400 + 100	7 à 10
(200)	6	1250	1250	1700	5.5 à 6
(113)	7	1300	2200	2500	8
(211)	7	1100	1350	300	3 à 4
(212)	2	250	170	200	0.7 à 1
(220)	2	350	350	650	1.4 à 2.6
(222)	2	60	200	370	0.2 à 1.5
(311) ; (302)	4	80 + 700	170 + 500	370 + 160	2 à 2.5

Dividing the calculated values by 250 (column 6), numbers are obtained, which clearly show that the sequence of the relative intensities, as calculated, is principally the same as that of the estimated ones.

in Fig. 4, and 5; evidently the centres of each pair are distant from each other 2,56 A.U., while the distance of a next pair in the same straight line is 3,86 A.U.; etc. Altough the arrangement of two immediately consecutive layers, such as *A* and *B* or *C* and *D* is essentially the same, each layer appears with respect to its neighbour turned round the *c*-axis over 90° and simultaneously shifted along a diagonal of (001) over a certain distance. As already mentioned, the smallest distance of the atomic centres is exactly that, which follows from W. L. BRAGG's values for the atomic radius of the *gallium*-atom: $2 \times 1{,}3$ A.U. $= 2{,}6$A.U. after BRAGG, while experimentally measured: 2,56 A.U. Four neighbouring atoms of one layer (cf. Fig. 5) are situated in the corners of a trapezium; just in its centre fits the *Ga*-atom of the immediately adjacent layer. If in the way indicated by BRAGG, round the atomic centra spheres be described with a radius $R = 1{,}3$ A.U., then the five spheres just mentioned appear to touch each other, so that in each double layer as *AB* or *CD*, all spheres are so closely packed, that the double layer could be thought to be built up completely by means of closest packed, massive spheres[1]). It may be remarked, moreover, that the atomic planes of { 110 } consist of three parallel ones, two of which have an identical atomic arrangement, the third being, however, at a different distance and having a somewhat different arrangement. If one considers the two

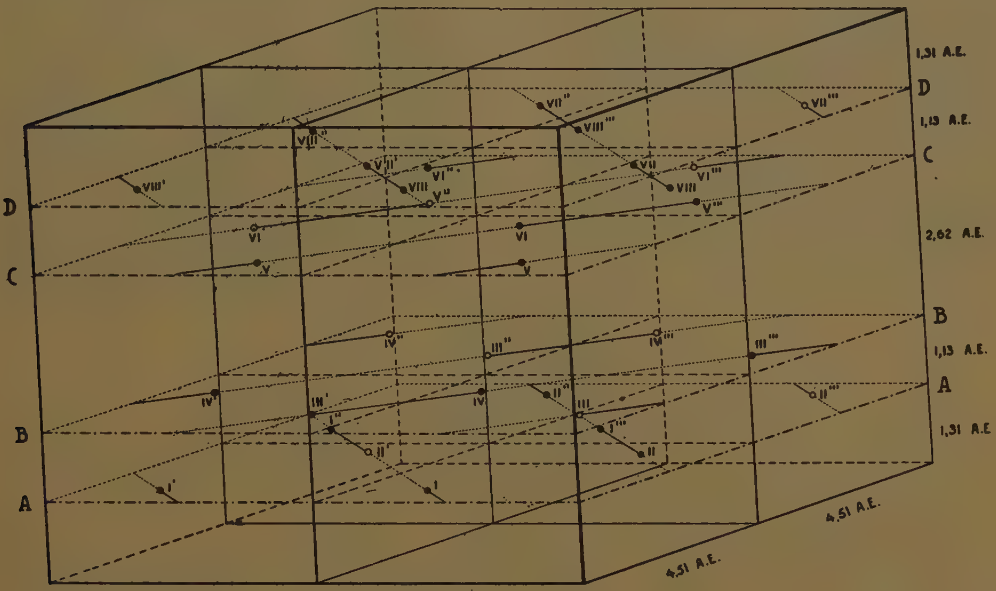

Fig. 4.

first, very closely approaching planes as a single one, the whole situation can also be described by saying, that in the directions (110), (110), etc. one *flat* plane of atoms interchanges with a plane, which appears to be slightly bent up and down in a regular way. It is this circumstance, which causes the intensities of { 110 } to get *not exactly* the value *zero*; calculation teaches, that there remains an extremely small intensity of the corresponding diffraction-images.

The atomic planes parallel to the basis {001} are, amongst all planes of the structure, those whose occupation by atoms is the densest.

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[1] Fig. 5 gives an orthogonal projection on (001) of two successive layers every time: Fig. 5*a* of *A* and *B*; Fig. 5*b* of *C* and *D*, which are identical with *AB*, but with respect to them turned round the *c*-axis over exactly 90°. The distance of two consecutive layers is: $\left(\frac{20}{40} - 2v\right) c_0 = \frac{6}{40} c_0 = 1{,}13$ A.U. The distance of an atomic centre in *B* to each of the nearest four centra in *A* is, in projection 2,3 A.U.; therefore, the true distance is: $\sqrt{(1{,}13)^2 + (2{,}3)^2} = 2{,}56$ A.U. From this follows, that the atomic spheres with a radius of 1,28 A.U. (according W. L. BRAGG) are situated in both layers in the way indicated in Fig. 5.

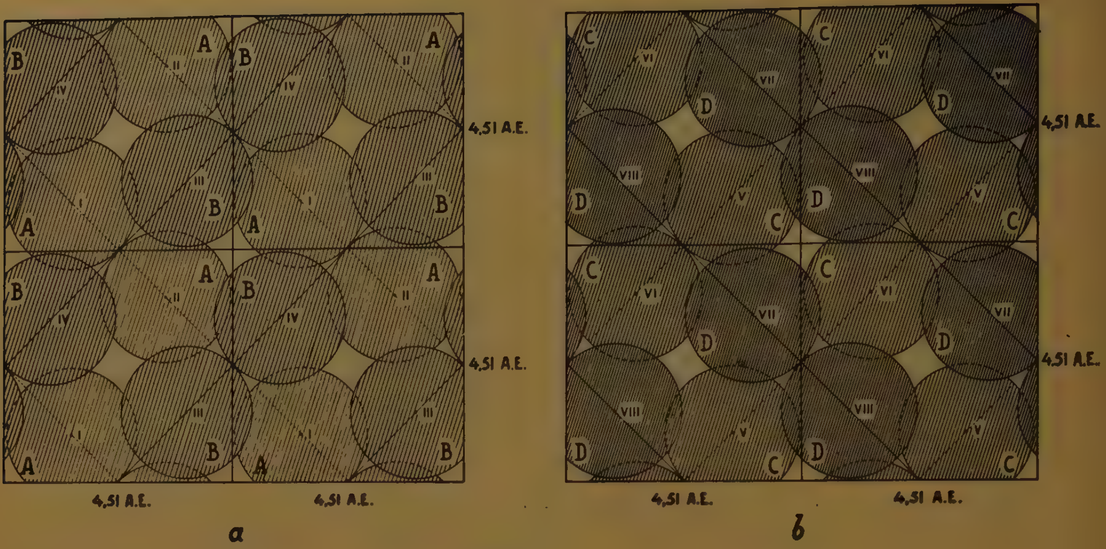

Fig. 5.

§ 20. It is remarkable, and highly in favour of the exactness of the here proposed structure of the metal, that from this structure several of the pecularities of the solid *gallium* may be deduced.

As becomes clear from the Fig. 3 and 4, the double layer *AB* parallel to {001}, is in the cell separated from the double layer *CD*, — which has the same structure as *AB*, but differs from it only by the fact that it is turned with respect to it round the *c*-axis over 90°, — by a free space between the atomic spheres. As the layer *C* is turned with respect to *A* over 90°, *C* cannot approach as near to the layer *B*, as *A* does: the atomic spheres would touch each other only, of the distance from *C* to *B* gets value: 2,48 A.U. (cf. Fig. 6; the sphere *V* must have the position *V'* to touch the layer *B*). In reality this distance is, however, 2,62 A.U., so that a free space of 0,14 A.U. remains open between *AB* and *CD*. To bring both double layers in touch with each other, the upper double layer would have to be pressed down over 0,14 A.U., — the height of the elementary cell then getting the value: 7,51 — 0,14 — 0,07 — 0,07 = = 7,23 A.U.

Now, as is already known since its discovery, the specific volume of solid *gallium* is *greater* than that of the liquid metal, — just as the specific volume of *ice* is greater than that of water at the same temperature. The idea is easily suggested now, that this peculiar behaviour of *gallium* is intimately connected with the decrease in volume, which the crystalline metal suffers in melting, because of the fact, that at the meltingpoint, the structure being broken up and the atoms regaining their free mobility, the free space between the atomic layers, mentioned above, will disappear at the same time.

Indeed, the specific weight of the *liquid gallium* can, on this supposition, be calculated from that of the *solid* metal, this being known as: 5,904. For, as the height of the cell is diminished from 7,51 A.U. to 7,23 A.U., this specific weight must change to: $\frac{7,51}{7,23} \times 5,904 = 6,124$; on the other hand, the specific weight of the *liquid gallium* actually observed is: 6,095. The difference between the calculated and observed numbers is only 0,5 %, — this being an agreement, which may be called really perfect.

Recently EHRENFEST[1]) drew attention to the fact that some analogies in behaviour also occur in the case of such metals as *bismuthum, antimony,*

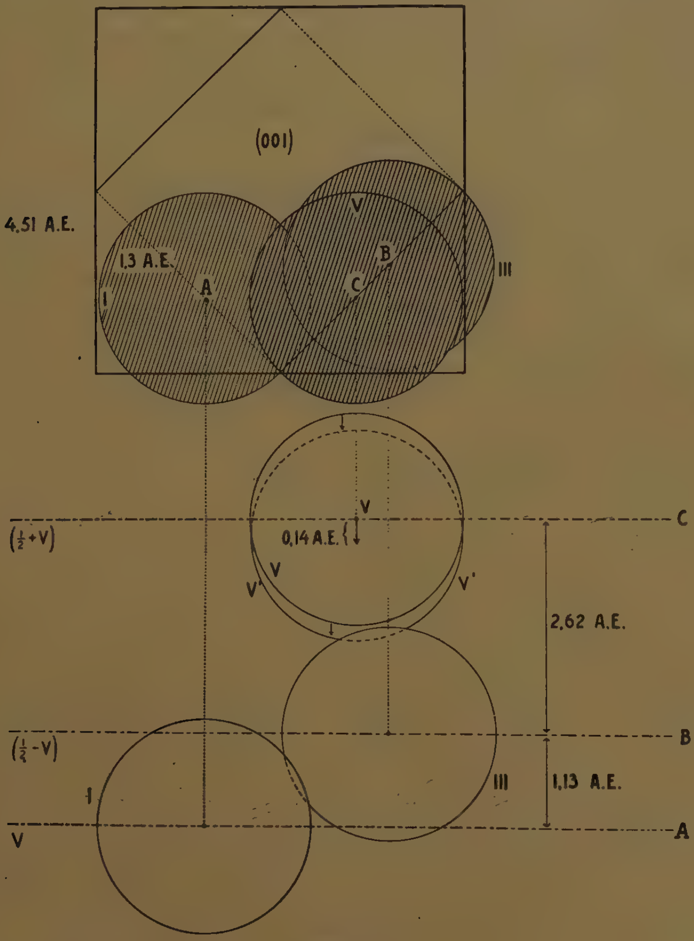

Fig. 6.

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[1]) P. EHRENFEST, Physica, 5, (1925), p. 383.

From the fact that *bismuthum* shows an extraordinarily great diamagnetic susceptibility, the author concludes that the electronic orbits which cause this phenomenon, must surround more than one atom of the structure; because of this fact, the importance becomes clear of these layers of atoms approaching each other very nearly. In *gallium* the distance between two such atoms (2,56 A.U.) is even smaller than in *bismuthum*. All three metals (*antimony* included) have in common, that their electric conductibility increases, as they melt; all three have a specific volume in the solid state greater than in the liquid condition.

etc., whose crystalstructure is, like that of *gallium*, characterised by the occurrence of such double layers of atoms very nearly approaching each other. Perhaps the occurrence of these double layers might be related to the other fact, that, such metals as *bismuthum, antimony*, and *gallium* also, form oxides, which according to circumstances, may show a weak basic or a weak acid function ($Ga(OH)_3$ with KOH and *ammonia; antimonites, antimonates, bismuthites*; etc.): it is e.g. imaginable, that *two* modifications of the atoms, depending on their momentaneous electronic configuration, should really take part in building up these crystalstructures, of which modifications one kind had a more "metallic" character and the other a nature more tending to that of a "metalloid"; *together* they would then be able to form such double layers of atoms approaching very nearly to each other.

§ 21. But also in other respects the proposed structure enables us to give a satisfactory account of the special phenomena observed with the solid metal.

Attention has already been drawn to the fact, that the crystals of *gallium* show *two* different habits, according as they are formed *rapidly* or *slowly* from the more or less undercooled molten mass. (page 1196; Fig. 1*a* and 1*b*). This phenomenon must be interpreted in this way, that there exists evidently a great difference in crystallisation-velocity with these crystals in different directions perpendicular to the different sets of atomic planes. Evidently this velocity perpendicular to (001) is, under comparable circumstances, much smaller than in directions perpendicular to faces of $\{111\}$ and $\{121\}$. As a consequence, if the crystal is only allowed sufficient time to develop, — i.e. in *slow* crystallisation, — the relative development of the faces of $\{001\}$ will increase gradually in comparison with that of forms, like $\{111\}$, $\{121\}$, etc. According to BRAVAIS, the faces predominantly developed in the crystal are generally those of *greatest* atomic density. That this is really the case here also, may now be immediately seen from the structure derived for the *gallium*: for in (001) the eight metal-atoms appear to be distributed over *four* planes *A, B, C* and *D* of the structure, each layer containing *two* atoms (Fig. 5); therefore, the density $\Delta_{(100)}$ of these planes is: $\frac{2}{a_0^2}=\frac{2}{20,34}=0{,}098$. On the other hand, for $\{111\}$ e.g., those 8 atoms are distributed over *six* planes, of which *four* contain only *one* atom, and *two* layers which have *two* atoms in a parallelogram. For $\{111\}$ the mean density of arrangement $\Delta_{(111)}$ is therefore: $\frac{4/3}{a_0\sqrt{2c_0^2+a_0^2}}=0{,}026$ only. Thus it is evident [1]) that, independent of the special values of the parameters *u* and v, *the density of the atomic arrangement parallel to* (001) *is about four times greater than that in the planes parallel to* {111}. It is evident for this reason, that the velocity of growth perpendicular to the atomic planes parallel to (001) is so much smaller than that in directions perpendicular to the planes of the form {111}; which involves, that the faces of this form must finally disappear, making gradually place for the more and more predominant form {001}. The specific density of the planes parallel to {121} is, moreover, again smaller, so that this form *à fortiori* will be absent in the crystals of Fig. 1^b. The bipyramidal habitus of the crystals of Fig. 1^a depends undoubtedly on the special properties of the strongly undercooled, liquid medium, from which they are generated; in many cases the degree of undercooling has, without any doubt, a great influence on the particular shape of the crystals, which are deposited from such a medium.

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[1]) It may be remarked, that the density of the atomic arrangement of $\{111\}$ and $\{001\}$ can only be *the same*, if the 8 atoms be distributed for $\{111\}$ over only *two* atomic planes. This occurs, if to *u* the value $^1/_4$ is attributed. This parameter-value, however, is excluded here, because in that case the intensity of the diffraction-images on the planes parallel to (121), must be *zero*, the spacings then being halved for this form. Experience, however, proves, that the planes parallel to $\{121\}$ have a great intensity.

Hitherto we have not been able to obtain sufficient information about the cleavability, the cohesion, the presence of gliding-planes, etc. of the *gallium*-crystals, in order to test also these properties by means of the here indicated crystalstructure; and the same is valid for some other physical properties, as e.g. thermic and electric conductibility; etc. Perhaps, however, it will appear possible to obtain before long, the data required to elucidate these phenomena also in the light of the crystalstructure deduced.

Groningen, Laboratory for Inorganic and
Physical Chemistry of the University.

Chemistry. — *"Some Remarks on the Crystalform of Boron-nitride and on the eventual Ambiguity in the Analysis of Powder-spectrograms."* By Prof. F. M. JAEGER and H. G. K. WESTENBRINK.

(Communicated at the meeting of September 25, 1926)

§ 1. *Boron-nitride*: $(BN)_x$ commonly occurs in the form of a white, tallowy powder, which in literature is described as amorphous[1]. Even on magnifying 500 times, no crystalform of the particles present in the powder studied[2] is observed under the microscope. There is no doubt, however, about the fact, that the compound is really microcrystalline; this was, a short time ago, experimentally proved for the first time by TIEDE and TOMASCHEK[3]. It is, however, impossible to provide better developed crystals by recrystallization from a solvent or molten mass, or by sublimation; therefore, on studying the substance by means of *X*-rays, it is *only* possible here to make use of powder-spectrograms after HULL-DEBIJE's method, without our having any opportunity to test the results obtained in any other way. In the following pages it is emphasized once more, how ambiguous results from the interpretation of such spectrograms may follow, if no other method in ROENTGEN-analysis can be made use of, or if neither goniometric measurements, nor sufficient data about the crystallographic symmetry are available for further control.

Another difficulty presented itself here in the fact, that the specific weight of the substance is not, or at least very inaccurately, known and its exact determination is much hampered by the peculiar nature of the compound. As the original preparation appeared to be not completely homogeneous under the microscope, but to contain small black grains, — it was necessary to separate these by fractional sedimentation with water. They consist principally of crystallized *boron*, which has a higher specific weight than the principal mass of the preparation. From the remaining mass about five fractions of a different degree of dispersion could be separated by fractional sedimentation; the last fraction gave with water a colloidal solution, from which the colloidal substance by addition of a trace of hydrochloric acid could be coagulated. After drying at 100° C., also this last preparation was studied in the same way: it appeared, however, that all preparations gave *identical* ROENTGEN-spectrograms. The specific weight of these different fractions, however, differed considerably and appeared to decrease with an increasing degree of division. Perhaps this fact might be related to the particular circumstance, that the molecular weight of *boron-nitride* is, according to most investigations, certainly a *multiple* of the most simple formula: BN; the dissociating power of the water may be the cause of the occurrence of a mixture of several kinds of such polymeric molecules. The last three fractions obtained showed finally only a small difference of their specific weights, so that its final value with near approximation could be fixed at $d_{4^0}^{18^0} = 1{,}99$. But as will become clear, this value presents again a new difficulty for the exact interpretation of the true crystalstructure.

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[1] L. MOESER and W. EIDMANN, Ber. d. d. chem. Ges., **35**, 536, 1902; A. STOCK and M. BLIX, Ber. d. d. Chem. Ges., **34**, 3039, (1901).

[2] W. H. BALMAIN, Phil. Mag. (3), **21**, 170, (1842); **22**, 467, (1843), **23**, 71, (1843); **24**, 191, (1844); Journ. für prakt. Chemie, **27**, 422, (1842); **30**, 14, (1843).

F. WÖHLER, Ann. der Chem. **74**, 70, (1850); Pogg. Ann., **79**, 467, (1851).

[3] E. TIEDE and H. TOMASCHEK, Zeits. f. Elektrochemie, **29**, 303, (1923); cf. also: E. TIEDE and F. BÜSCHER, Ber. d. d. chem. Ges., **53**, 2206, (1920).

§ 2. A considerable number of diffraction-lines could be observed on the well developed spectrograms, which were obtained after HULL-DEBIJE's method in using the K-radiation of a *copper*-anticathode. The lines showed strongly different intensities on the film. The principal ones are reviewed in the following table; assuming a *cubic* symmetry as the most probable one in respect to the chemical composition, the indices were calculated from the suitable quadratic equation. Such a cubic arrangement may a priori be considered as probable here, taking

TABLE I.

Number of the lines:	Intensity:	Double distance to the centre in mm:	$\sin^2\frac{\theta}{2}$:	Calculated values of $\sin^2\frac{\theta}{2}$:	Indices: (MILLER)
1	9	18.0	0.0321	0.0321	(111)
3	10	23.5	0.0542	0.0535	(102)
4	3	25.8	0.0651	0.0642	(112)
5	4	36.5	0.1275	0.1284	(222)
6	3	38.7	0.1425	0.1391	(320)
8	4	48.4	0.2166	0.2140	(420)
9	1	52.1	0.2477	0.2568	(422)
12	4	66.4	0.3794	0.3852	(600)

Quadratic equation: $\sin^2\frac{\theta}{2} = 0.0107\,(h^2 + k^2 + l^2)$ (α-radiation).

$R = 25$ mm. For the lines N⁰. 2 and 7, cf. Table II.

Tension: 55000 Volt; time of exposure: 6 hours.

into consideration the relatively small difference in atomic number of the *boron-* and *nitrogen*-atoms [1]).

From the indices of the scattering atomic planes, which evidently occur in all possible combinations of odd and even numbers, it follows, that the underlying grating is a *simple cubic* one, the characteristic translation of it (edge of the cubic cell) a_0 being calculated, with respect to the wave-length used, as 7,44 A.U. But from the value for $d = 1{,}99$, the number n of molecules *BN* present in such a cell, results as:

$$n = \frac{(7{,}44)^3 \times 1{,}99 \times 10^{-24}}{1{,}64 \times (11 + 14) \times 10^{-24}} = 20.$$

Therefore, within each cell 20 *boron-* and 20 *nitrogen*-atoms should necessarily find their places, — a number, which can hardly be considered to be in accordance with that of the equivalent positions, characteristic for the space-groups of cubic symmetry.

§ 3. However, as follows from Table II, the results of the measurements can be interpreted with the same degree of accuracy, also on the assumption, that here a *tetragonal* grating is present. (See Table II following page).

Supposing *this* interpretation to be the right one, *boron-nitride* appears to be tetragonal, with a grating built up from *simple tetragonal cells.* The edges of the cell are: $a_0 = 4{,}295$ A.U. and $c_0 = 5{,}176$ A.U.; so that the axial ratio has the value: $a : c = 1 : 1{,}2052$. If again the value of d_0 at 18° C. be considered as: 1,99, the number n of molecules *BN* per elementary cell is calculated as: $n = \frac{(4{,}295)^2 \times 5{,}176 \times 1{,}99 \times 10^{-24}}{1{,}64 \times 25 \times 10^{-24}}$ $= 4{,}6$; so that 4 or 5 *boron*-atoms and the same number of *nitrogen*-atoms must be present in each cell. The first number is certainly, but the second not in accordance with the number of equivalent positions compatible with the special symmetry of the tetragonal space-groups.

§ 4. As all further necessary data are lacking, it is impossible here to fix our choice and to decide, whether *boron-nitride* has *cubic or tetragonal* symmetry. An analogous case of ambiguity in the interpretation of powder-spectrograms occurred recently in the study of *thallium* by LEVI [2]). This author attributed to the metal, with respect to his results obtained by the HULL-DEBIJE-method only, a hexagonal structure (trigonal closest packing), with the grating-constants: $a = 3{,}47$ A.U.; $c = 5{,}52$ A.U.; and $a : c = 1 : 1{,}59$. TERPSTRA [3]) drew, however, attention to the fact, that

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[1]) The case of a trigonal structure, which could be supposed, appeared only to be compatible with the results of the measurements, if the axial ratio were $a : c = 1 : 1{,}225$. Then, however, α must be 90°, and no difference is present then with a cubic grating, considered in the direction of a trigonal symmetry-axis.

[2]) G. R. LEVI, Nuovo Cimento, May, June, (1924); Zeits. f. Kryst. **61**, 561, (2925).

[3]) P. TERPSTRA, Zeits. f. Kryst. **63**, 318, (1926).

TABLE II.

Number of the lines:	Intensities (estimated)	Double distance to the centre in mm:	$\theta/2$:	$\sin^2\frac{\theta}{2}$:	$\sin^2\frac{\theta}{2}$:	Calculated values of $\sin^2\frac{\theta}{2}$:	Indices (MILLER):	Remarks:
1	9	18.0	10°19′	0.1791	0.0321	0.0321	(100)	
2	2	21.2	12°9′	0.2105	0.0443	0.0442	(101)	β-line.
3	10	23.5	13°28′	0.2329	0.0542	0.0542	(101)	
4	3	25.8	14°47′	0.2552	0.0651	0.0642	(110)	Only present on one film.
5	4	36.5	20°55′	0.3570	0.1275	0.1284	(200)	
6	3	38.7	22°10½′	0.3774	0.1425	0.1505	(201)	
7	2	43.8	25°6′	0.4242	0.1799	0.1768	(202)	β-line.
8	4	48.4	27°44′	0.4654	0.2166	0.2168	(202)	
9	1	52.1	29°51′	0.4977	0.2477	0.2489	(212)	
10	1	63.9	36°37′	0.5965	0.3558	0.3586	(321)	β-line.
11	3	65.8	37°42′	0.6115	0.3740	0.3773	(302)	Only observed on one film.
12	4	66.4	38°3′	0.6164	0.3799	0.3857	(104)	
13	5	71.8	41°8′	0.6579	0.4327	0.4394	(321)	
14	1	76.4	43°46′	0.6917	0.4785	0.4878	(303)	Only present on one film.
15	3	87.9	50°22′	0.7701	0.5931	0.5999	(331)	

Quadratic form: $\sin^2\frac{\theta}{2} = 0.0321\,(h^2+k^2) + 0.0221\,l^2$ (α-radiation);

and $\sin^2\frac{\theta}{2} = 0.0262\,(h^2+k^2) + 0.0180\,l^2$ (β-radiation).

$R = 25$ mm. Tension: 55 Kilovolt; time of exposure: 6 hours.
Line N⁰. 2 is the β-image of N⁰. 3; line 7 that of N⁰. 8; N⁰. 10 that of N⁰. 13; all other lines are α-images.

these observations of $\sin^2\frac{\theta}{2}$ could as well, if not better, be calculated from a quadratic equation for a tetragonal grating, whose parameters are: $a_0 = 5{,}2$ A.U. and $c_0 = 8{,}2$ A.U. Only after the Italian author¹) had recently been able to obtain LAUE-spectrograms of cathodically deposited, very small *thallium*-crystals, it was possible for him to prove beyond any doubt, that the symmetry is certainly *hexagonal*. As the calculated and observed intensities for the structure of *thallium* attributed by him,

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¹) G. R. LEVI, „Nuovo Cimento", October (1926).

do not agree, however, a reviewed investigation of this crystalstructure remains highly desirable.

These data and those given in this paper, may, therefore, be once more considered as a warning, not to draw conclusions about crystalstructures, where *only* the results of powder-spectrograms can be used. If it is required to give a final solution of problems concerning the crystalstructure of the compounds investigated, such data can only be considered as valuable, if used in connection with the results of other spectrographic methods and of crystallographic measurements.

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Physical Chemistry of the University.

Chemistry. — *"The Space-Groups of the Rhombic and Monoclinic Heptahydrates of the Sulphates of the bivalent Metals."* By H. G. K. WESTENBRINK. (Communicated by Prof. F. M. JAEGER.)

(Communicated at the meeting of September 25, 1926).

§ 1. The *heptahydrates* of the bivalent metals: *zinc, iron, magnesium,* etc., can form isomorphous or isodimorphous series of mixed crystals. For some of them the stable form has rhombic-bisphenoïdal symmetry, for others the monoclinic-prismatic forms are the stabler ones.

The rhombic modification of $MgSO_4$, $7H_2O$, of $MgCrO_4$, $7H_2O$, of $ZnSO_4$, $7H_2O$ and of $NiSO_4$, $7H_2O$ were obtained by slow evaporation at roomtemperature of their solutions in water. Their habit is always strongly elongated in the direction of the *c*-axis. Far predominant is the prism $\{110\}$; of the three pinacoids only $\{010\}$ occurs. The experiments described in the following pages were chiefly made with the *magnesium*-salt; the properties of the other members of this series differ, however, only immaterially from those of the *magnesium*-salt, so that the conclusions drawn in that case, may safely be extended to the other salts.

For the determination of the identity-distances I in the three principal directions, three rotation-spectrograms were prepared, in which the crystal was successively rotated round the *c*-, the *a*- and the *b*-axis. In these experiments a flat photographic plate was made use of. The results obtained are reviewed in table I.

TABLE I.
(Distance of crystal to plate: 40 mm)

Axis of revolution:	Measured distances between the hyperbolae 0 and 1:	Identity-distances in the direction of the axes:
c [1]	9.5 mm	c_0 [1] $= 6.7$ A.U.
b	5 mm	$b_0 = 13.0$ A.U.
a	5 mm	$c_0 = 13.0$ A.U.

The data for a_0, b_0 and c_0 in this table give only the *order of magnitude* of the required distances, not their exact values. To get more accurate data for the dimensions of the elementary cell, BRAGG-spectrograms for the best developed faces of $\{110\}$ were studied. The exact distance from plate to crystal was determined in this case by simultaneously photographing the spectrum on $\{100\}$ of a piece of *rock-salt*. The spacings $d_{(110)}$ could in this way be determined with an accuracy of circa 0,02 A.U., when the distance between plate and crystal happened to be 60 mm. The value of $\frac{\theta}{2}$ for the most intense line of $MgSO_4, 7\,H_2O$ was found to be: 10°30′ if *copper-K_α*-radiation of 1,540 A.U. was used here. The quadratic equation in the rhombic system having the form:

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[1] The axial ratio is expressed by: $a:b:c$; the dimensions of the elementary cell in the corresponding directions are indicated by a_0, b_0 and c_0.

$$sin^2\frac{\theta}{2}=\frac{\lambda^2}{4\,a_0^2}h^2+\frac{\lambda^2}{4\,b_0^2}k^2+\frac{\lambda^2}{4\,c_0^2}l^2,$$

this equation becomes in the case that the said interference-image is supposed to be one of the 2^{nd} order $(h=k=2)$:

$$sin^2\,10°30'=\frac{(1{,}540)^2}{a_0^2}+\frac{(1{,}540)^2}{b_0^2};$$

for the planes parellel to $\{110\}$.

From the very accurately known axial ratio: $a:b:c=0{,}9901:1:0{,}5709$, it may be, moreover, deduced, that $a_0=0{,}9901\,b_0$, and therefore: $b_0=12{,}01$ A.U.; so that $a_0=11{,}89$ A.U. and $c_0=6{,}86$ A.U. respectively.

It is, of course, à priori not quite sure, that $a_0 : b_0 : c_0$ is equal to $a : b : c$; but certainly $a_0 : b_0 : c_0$ may be supposed to be equal to: $ma : nb : pc$, in which ratio m, n, and p are integer numbers. But from the rotation-spectrograms it could here be deduced already, that $m=n=p=1$ in this case.

If V be the volume of the elementary cell ($=12{,}01\times11{,}89\times6{,}86$ A.U.^{3}); s the specific weight: 1,677, and M the molecular weight of the *magnesium*-salt; 246,49, — then the number N of molecules per elementary cell is calculated to be:

$$N=\frac{V\times s}{1{,}64\times M\times10^{-24}}=4{,}06,$$

i.e. four molecules of the hydrated salt.

§ 2. For the identification of the interference-images the rotation-spectrogram obtained by rotating the crystal round the *c*-axis, appeared to be the most suitable one. As a_0 is practically equal to b_0, instead of the rigorous quadratic formula:

$$sin^2\frac{\theta}{2}=0{,}00419\,h^2+0{,}00411\,k^2+0{,}01260\,l^2 \text{ (for } K_{(\alpha)}\text{-radiation)}$$

the simplified equation:

$$sin^2\frac{\theta}{2}=0{,}0041^5\,(h^2+k^2)+0{,}0126\,l^2$$

could be used in the analysis of the spectrograms.

In table II the calculated and observed values for $sin^2\frac{\theta}{2}$ are put

TABLE II.				
(Distance of crystal to plate: 39 mm)				
MILLERian Symbol:	$Sin^2\frac{\theta}{2}$ (calculated):	Distance to the centre:	$Sin^2\frac{\theta}{2}$ (observed):	
(200)	0.0166	10.— m,m.	0.0157	Principal spectrum
(210)	227	13.— „	256	
(220)	332	14.5 „	314	
(300)	373	—	—	
(310)	415	16.5 „	395	
(320)	539	19.5 „	528	
(330)	587	—	—	
(400)	664	22.5 „	670	
(410)	705	23.7 „	728	
(420)	830	—	—	
(430)	0.1037	30.2 „	0.1050	
(440)	1328	—	—	
(500)	1037	—	—	
(510)	1079	—	—	
(520)	1203	32.5 „	1160	
(530)	1411	37.5. „	1400	
(600)	1494	—	—	
(101)	0.0168	—	—	1st Accessory spectrum
(111)	210	11.5 „	0.0204	
(201)	294	14.5 „	314	
(211)	336	—	—	
(221)	462	—	—	
(301)	504	19.— „	505	
(311)	546	20.— „	552	
(321)	672	22.5 „	670	
(331)	882	—	—	
(401)	798	25.— „	791	
(411)	840	26.— „	840	
(421)	966	28.— „	938	
(431)	0.1176	32.— „	0.1301	
(441)	1470	—	—	
(501)	1176	32.— „	1130	
(511)	1218	—	—	
(521)	1344	36.5 „	1350	
(531)	1554	—	—	

TABLE II *(Continued).*

(Distance of crystal to plate 39 mm)

MILLERian Symbol:	$Sin^2 \frac{\theta}{2}$ (calculated):	Distance to the centre:	$Sin^2 \frac{\theta}{2}$ (observed):	
(102)	0.0546	—	—	2nd Accessory spectrum
(112)	588	20.5 m.M.	0.0574	
(202)	672	23.— „	693	
(212)	714	—	—	
(222)	840	26.— „	840	
(302)	882	—	—	
(312)	924	—	—	
(322)	0.1050	30.— „	0.1037	
(332)	1260	—	—	
(402)	1176	—	—	
(412)	1218	—	—	
(422)	1344	36.— „	1326	
(432)	1554	41.— „	1554	
(442)	1848	—	—	
(502)	1554	41.— „	1554	
(512)	1596	—	—	
(522)	1722	44.5 „	1704	
(532)	1932	—	—	
(103)	1176	32.— „	1135	3rd Accessory spectrum
(113)	1218	—	—	
(203)	1302	—	—	
(213)	1344	37.— „	1373	
(223)	1470	39.— „	1465	
(303)	1512	40.— „	1510	
(313)	1554	—	—	
(323)	1680	43.5 „	1663	
(333)	1890	49.— „	1888	
(403)	1806	—	—	
(413)	1848	48.— „	1846	
(423)	1974	—	—	
(433)	2184	—	—	
(443)	2478	—	—	
(503)	2184	—	—	
(513)	2226	58.— „	2209	
(523)	2352	—	—	

together, with the corresponding MILLERian symbols eventually multiplied by the order *n*. Of these indices the numbers *h* and *k* can here, if desired, be interchanged. Only the diffraction-lines for K_a-radiation are reviewed in the table; to show with what accuracy the indices can be attributed to the observed lines, also some values of $sin^2 \frac{\theta}{2}$ of lines not observed in the spectrograms are included with the other ones.

From table II it becomes clear that no certainty is obtained, whether the observed lines correspond to (201) or (211) and to (202) or (212). A slight difference in the measured distance between plate and crystal has here a relative great influence on the values of $sin^2 \frac{\theta}{2}$. But leaving these uncertain values aside for the moment, it becomes in every case evident, that a number of lines occur, for which $(h + k)$ is *odd*; so e.g.: (210), (410), (430), (520), (301), (321), (411), (431) or (501), (521), (322), (432), (522), (213), (303), (323) and (413); moreover, such for which $(h + l)$, as well as $(k + l)$ are *odd*[1]): (310), (530), (401), (421), and (223); in the third place such lines, for which $(h + k + l)$ is an *odd* number, e.g.: (210), (410), (430), (520), (111), (311), (401), (421) and (223).

From this it becomes sufficiently certain, that the underlying type of grating can be no other than that built up by *simple rhombic cells.*

This conclusion is contradictory to an hypothesis made by JACKSON [2]) concerning his results of the study of paramagnetism of these sulphates at low temperatures. According to this hypothesis, the type of grating present here should be that with body-centred cells. But if this were true, the intensities of all diffraction-images for which $(h + k + l)$ is *odd*, should appear to be systematically equal to *zero*. As becomes clear from the above, this is not the case, there being, therefore, no reason to sustain the hypothesis mentioned.

§ 3. There are *four* rhombic-bisphenoïdal space-groups, which, in WYCKOFF's notation, are discerned as V_1, V_2, V_3 and V_4 and which have, therefore, the symmetry-elements of structures built up by intercalated BRAVAIS' gratings with simple rhombic cells. Of these space-groups V_1 has only axes of rotation; V_2 rotatory axes parallel to the directions [100] and [010] and screw-axes parallel to the direction [001]; V_3 possesses rotatory axes parallel to [100] and screw-axes parallel to [001] and [010]; finally V_4 has only screw-axes. Now from the spectrograms after BRAGG's method, obtained for (100), (010) and (001), it followed already that the *odd* orders of the diffraction-images on these planes have all the intensity *zero*. Therefore, *all* spacings of the planes parallel to the three pinacoids are evidently halved by the other planes. The only space-group possible here can, as a consequence, be no other than V_4.

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[1]) As a_0 and b_0 are approximately identical, *h* and *k*, and also $(h + l)$ and $(k + l)$, cannot be discerned from each other.

[2]) L. C. JACKSON and H. KAMERLINGH ONNES, Phil. Trans. Royal Soc., *A*, **224**, 1, (1924).

Table III gives a review of the measured distances $d_{(110)}$, from which values the dimensions a_0, b_0 and c_0 and the specific weight are calculated, with the use of the accurately known axial ratio [1]).

TABLE III.

Salts:	$d_{(110)}$:	Axial ratio $a:b:c$:	a_0	b_0	c_0	Specific weight (calculated):	Specific weight (literature):
$MgSO_4$, 7 H_2O	8.45	0.9901 : 1 : 0.5709	11.89	12.01	6.86	1.717	1.677
$MgCrO_4$,7 H_2O	8.45	0.9901 : 1 : 0.5735	11.89	12.01	6.89	1.827	1.695
$NiSO_4$, 7 H_2O	8.46	0.9804 : 1 : 0.5631	11.86	12.08	6.81	1.882	1.953
$ZnSO_4$, 7 H_2O	8.46	0.9815 : 1 : 0.5656	11.85	12.09	6.83	1.933	1.974

§ 4. *The monoclinic modification.* The stabler form, e.g. of $FeSO_4$, 7 H_2O, of $CoSO_4$, 7 H_2O, etc., which were the only salts suitable for the following experiments, is monoclinic-prismatic. The flat crystals of $FeSO_4$, 7 H_2O ordinarily grow out on a face of {001}, this form, therefore, always being predominant. The *cobalto*-salt crystallizes mostly with predominant development of $\{\bar{1}01\}$. Most experiments were made with the *iron*-salt. The results of the analysis of three rotation-spectrograms, in which the crystal was successively rotated round the *a*-, the *b*- and the *c*-axis, are reviewed in table IV.

TABLE IV.
(Distance of plate to crystal: 40 mm)

Axis of revolution:	Distance of the first hyperbolae to centre:	Identity-distances:
a-axis	4 mm	$a_0 = 15.50$ A.U.
b-axis	4.75 mm	$b_0 = 13.07$ A.U.
c-axis	3 mm	$c_0 = 20.60$ A.U.

For the accurate measurements of the grating-constants a spectrogram after BRAGG's method was made on (001), this plane being the best suited for that purpose. On this spectrogram was found one line belonging to the $FeSO_4, 7\,H_2O$ besides the lines of *rocksalt*, which were simultaneously photographed. Supposing that this line is respectively of the 1st, 2nd, 3rd and 4th order, the results obtained in all these cases are reviewed in table V.

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[1]) The axial ratios and specific weights are taken from: P. GROTH, "Chemische Krystallographie", (1908), Volume II.

TABLE V.

Order number n:	$d_{(001)} = \dfrac{n\,.\,\lambda}{2\sin\dfrac{\theta}{2}}$:	c_0 1) $= \dfrac{d_{(001)}}{\sin 104^\circ\,15^1/_2{}'}$:
1	4.85 A.U.	5.00^5 A.E.
2	9.70 A.U.	10.01 A.E.
3	14.55 A.U.	15.01^5 A.E.
4	19.40 A.U.	20.02 A.E.

From this table it becomes evident, that the identity-distance in the direction of the c-axis becomes really equal to the value found by means of the rotation-spectrogram, if calculated on assuming it to be of the *fourth* order. To eliminate each doubt about this, attempts were made, by much longer exposure, to photograph the lines of lower order, their places on the plate now being exactly known. But no traces of one of these lines was ever observed. As the axial ratio of the monoclinic $FeSO_4, 7\,HO_2$ is: $a:b:c = 1{,}1828:1:1{,}5427$, the distances c_0, a_0 and b_0 were calculated to be: $c_0 = 20{,}02$ A.U.; $a_0 = 15{,}34$ A.U. and $b_0 = 12{,}98$A.U.

The number N of molecules per unit-cell was then calculated by: $N = \dfrac{V \times s}{M \times 1{,}64\,.\,10^{-24}} = 16$; in this formula $V = 15{,}34 \times 20{,}02 \times 12{,}98 \times \times \sin 104^\circ 15\tfrac{1}{2}{}'$; $s = 1{,}899$ and $M = 278{,}01$.

The quadratic equation in the monoclinic system can be written:

$$\sin^2\frac{\theta}{2} = \frac{\lambda^2}{4\,a_0^2\,\sin^2\beta}\,h^2 + \frac{\lambda^2}{4\,c_0^2\,\sin^2\beta}\,l^2 - \frac{\lambda^2\cos\beta}{2\,a_0\,c_0\,\sin^2\beta}\,hl + \frac{\lambda^2}{4\,b_0^2}\,k^2.$$

Using K_α-copper-radiation, the coefficients for $FeSO_4, 7\,H_2O$ can be easily calculated and the formula becomes:

$$\sin^2\frac{\theta}{2} = 0{,}00268\,h^2 + 0{,}00158\,l^2 + 0{,}00101\,hl + 0{,}00352\,k^2.$$

The coefficients in it are, however, so small, that by its aid the indices cannot be attributed to the diffraction-lines with sufficient accuracy. But

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1) The obtuse angle β between c- and a-axis is in the case of the *iron*-salt: $104^\circ 15^1/_2{}'$.

yet notwithstanding this inconvenience, the space-group could be determined in this special case in the following way.

§ 5. The simple monoclinic grating Γ_m is the fundament of 4 of the 6 spacegroups of monoclinic-prismatic symmetry: C^1_{2h}, C^2_{2h}, C^4_{2h} and C^5_{2h}. In each elementary cell of these four space-groups never more than 4 equivalent points are present. The two remaining space-groups: C^3_{2h} and C^6_{2h} are built up by means of the BRAVAIS' grating Γ'_m, the centre of the planes (001) of its elementary cells being also occupied by a point. In these unit-cells no more than 8 equivalent points can be present. As the choice of the angle β in the monoclinic system is arbitrary within certain limits, this grating can also be considered as being built up by means of cells of the type Γ'''_m, which is characterized by the fact, that *all* faces of it are centred. In such an elementary cell 16 equivalent positions can be present indeed. The monoclinic $FeSO_4$, HO_2, having 16 molecules per cell, must, therefore, belong to one of the space-groups C^1_{2h} or C^6_{2h}. Now it was found, that the 1st, 2nd and 3rd order images on (001) have the intensity *zero*: the space-group C^6_{2h}, therefore, appears to be the only possible one, because only there the spacings between the planes (001) of the grating Γ'''_m are really *quartered* by other atomic planes, as a consequence of the presence of gliding-mirrorplanes. The edges of the elementary cell Γ'''_m coïncide with the ordinary crystallographic axes: although the edges of the smallest elementary cell Γ'_m, therefore, do *not* coïncide with those axes, it appears, however, unnecessary to make another choice of the coördinate-axes here. If the crystals were placed in such a position as to make the edges of the cells Γ'_m coïncide with the crystallographic axes, it would appear, by using LEWIS' transformation-formule [1]), that e.g. the form $\{110\}$ would get the symbol: $\{\bar{2}21\}$. As the faces of $\{110\}$ are predominant, the more complicated indices for them are not feasible; so that the new choice of axes can hardly be considered as an advantageous alteration.

In the case of $CoSO_4$, $7\,H_2O$, whose axial ratio is:

$$a:b:c = 1{,}1815:1:1{,}5325, \text{ with } \beta = 104^\circ 40',$$

the spacing $d_{(001)}$ was found to be: 19,39 A.U. From this it follows, that:

$$c_0 = 20{,}04 \text{ A.U.};\ a_0 = 15{,}45 \text{ A.U. and } b_0 = 13{,}08 \text{ A.U.}$$

The specific weight of the salt is, from these data, calculated at: 1,889; by GOSSNER and PETTERSON values were found between 1,948 and 1,964, a result which may be considered to be in sufficient agreement with the calculated value, concerning the rather appreciable inaccuracies of the measurements of these authors.

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[1]) Cf. F. M. JAEGER, „*Inleiding tot de Studie der Kristalkunde*", Groningen, (1924), p. 66.

§ 6. *Comparison of the monoclinic and rhombic gratings with each other.* Both types of structures may be best compared in considering together the simple rhombic cell on the one hand, and the monoclinic cell of type Γ_m' on the other hand. The data required are taken from the observations with the rhombic *magnesium-* and the monoclinic *iron-*salts.

In table VI these numbers are reviewed:

TABLE VI.

	Rhombic grating:	Monoclinic grating:
a_0	11.89 UA..	15.34 A.U.
b_0	12.01 A.U.	12.98 A.U.
c^0	6.86 A.U.	20.02 A.U.

In Fig. 1 the projection is given of the elementary cells of the BRAVAIS' gratings Γ_m'' and Γ_m''' on the plane (010). $AB = 15{,}34$ A.U.; $BC = 20{,}02$ A.U.; $\angle ABC = 104°15\frac{1}{2}'$. From this follows: $DB = 22{,}02$ A.U. and $BE = 11{,}01$ A.U. The length of the perpendicular AG, which is drawn from A to BD, is calculated to be: 13,32 A.U.; therefore, $\frac{1}{2} AG = 6{,}66$ A.U.

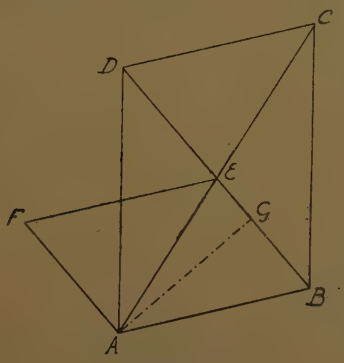

Fig. 1.

Now the dimensions BE and $\frac{1}{2} AG$ appear to be almost identical with a_0 and c_0 of the rhombic cells, while also b_0 has in both cases values which differ only slightly. If, therefore, BE be called: c and $\frac{1}{2} AG$ in the same way: a, — then the corresponding distances in both cases may be compared as is done in Table VII:

TABLE VII.

Rhombic grating:	Monoclinic grating:
$a_0 = 11.89$ A.U.	$c_1 = 11.01$ A.U.
$b_0 = 12.01$ A.U.	$b_0 = 12.98$ A.U.
$c_0 = \;6.86$ A.U.	$a_1 = \;6.66$ A.U.

Suspicion arises, that both structures may be transformed into each other by relatively small translations and rotations only. If, therefore, a yet closer comparison be required, it appears feasible to put both gratings in such positions with respect to each other, as is drawn in Fig. 2.

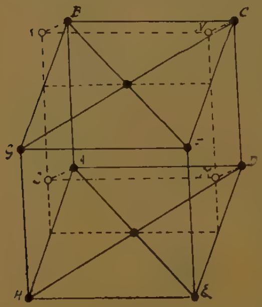

Fig. 2.

In this figure *ABCDEFGH* is the monoclinic cell (Γ''_m); the lines *KL* and *NM* divide the faces *ABGH* and *DCFE* into two equal parts; $\angle HAB = 119°42'$; and $\angle LAB = 90°$. The parallelopipedon *ABCDMNKL* now is almost the same as the rhombic cell, the original *a*-axis of it having the position *AB*, and the original *c*-axis the position *AL*.

Finally in table VIII a review is given of the values of the so-called "molecular-volumes", i.e. of the volumes of the elementary cells, divided by the number of molecules present in each of them:

TABLE VIII.

Salts:	Modification:	Molecular volume in A.U.^{3}:
Mg-sulfate	Rhombic	244.9
Mg-chromate	"	245.9
Ni-sulfate	"	243.9
Zn-sulfate	"	244.7
Fe-sulfate	Monoclinic	241.4
Co-sulfate	"	244.8

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Palæontology. — *"Manis Palaejavanica, the Giant Pangolin of the Kendeng Fauna."* By Prof. EUG. DUBOIS.

(Communicated at the meeting of October 30, 1926).

Near Kedung Brubus, 40 km E.S.E. of Trinil, in the same tract of the Kendeng formation from which a piece of a very peculiar human mandible had been obtained, which, on closer consideration, after the discovery of a lower premolar at Trinil, I have ascribed to Pithecanthropus erectus, I found, almost two years later, a number of bones of a gigantic Manis species.[1]) In all I found 28 bones or large pieces of bones, some of them coherent, still in their natural mutual position or only very little dislocated. They all were spread over an area of a few square meters, and as regards form, bear a striking resemblance to the homonymous bones of the present Manidae. They are certainly parts of one skeleton of a Manis species and agree most closely with Manis javanica Desm., with this difference that the dimensions are truly gigantic. The long bones of the hand and the foot are, indeed, more thickly built, comparatively short for their length, which, it seems, must be ascribed to the claws being necessarily relatively stronger in a so much heavier species. But yet from what is available (among which also pieces of vertebrae and of the skull) the total length of the animal may be estimated to have been at least $2^1/_2$ meters, i.e. three times the length of a middle-sized Javanese pangolin, and more than once and a half that of a fairly sized adult existing Giant Pangolin of West Africa. The specimen found was, besides, not even entirely full-grown, as appears from the fact, that the epiphyses of the ulna, the radius, the femur, the tibia, and the calcaneus have not yet entirely united with the body of the bone.

I have called the species Manis palaejavanica[2]), denoting by this name the closer relationship with the Javanese species of to-day, from which it is, however, very well to be distinguished by characters of minor importance.

The available parts of the skeleton[3]) are:

1. A considerable piece of the left *temporal bone* with the processus zygomaticus, in connection with a large part of the *frontal bone* and a small piece of the *parietal bone* with its antero-inferior angle. (Plate, middle row, third figure from the left. Above this a skull of M. javanica).

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[1]) Verslag van het Mijnwezen over het 2e Kwartaal 1892. Batavia. Landsdrukkerij. 1892.

[2]) EUG. DUBOIS, Das geologische Alter der Kendeng- oder Trinil-Fauna. Tijdschrift van het Kon. Ned. Aardrijkskundig Genootschap, 2nd Series, Vol. 25. (1908), p. 1267.

[3]) Belonging to the Collection-DUBOIS of the Leyden University.

The breadth of the processus zygomaticus, immediately before the place of the lost tympanicum, is 20.5 mm; the corresponding breadth of the skeleton of Manis gigantea Ill. in the Rijks Museum van Natuurlijke Historie at Leyden (Cat. N⁰. 3) is 14.3 mm, and of that of a more than middle-sized Manis javanica Desm., in my possession, 10 mm.[1] The length of the sutura fronto-temporalis is 25 mm, in the Manis gigantea it is 20 mm, and in the more than middle-sized Manis javanica 14.5 mm. In this it should be considered that from species to species the size of the neurocranium does increase relatively less than the size of the body. The plaster cast of the available part of the endocranial surface shows sharp separation of the lobus olfactorius, very pronounced folding of the pallium, especially in the lobus hippocampi, which is large also here, and in the parts lying before this, to the lobus olfactorius — undoubtedly as a consequence of the large size of the body —, further a very remarkable wide and deep depression, which implies a considerable deficiency of brain mass, round the place where the fossa Sylvii of the Manidae was described. The bone wall of the cranial vault is thickened there to 9.3 mm, on account of local smaller *growth of the brain* (for the outer surface of the skull is smooth, and there is no mechanic cause for this growth of the bone), whereas behind it, at the thinnest place of the fragment, only 5 mm can be measured. An endocranial plaster cast of M. javanica shows a similar condition, only the folding and also the depression of the cerebral surface are not so considerable — no doubt on account of the smaller body size; the depression, especially, is comparatively less wide. The thickness of the bone wall reaches there a maximum of 3.6 mm, and behind it, at the thinnest place, it is scarcely 1 mm.

It seems that from the local shortage of brain mass described for M. palaejavanica, it is justifiable to conclude that also this pliocene giant species was covered with scales.

2. A piece of the right half of the *occipital bone*, round the asterion in connection with a piece of the *parietal bone* at its postero-inferior angle, and a piece of the *temporal bone* at its postero-superior angle. The inner side shows the dividing ridge between the pallium and the cerebellum.

3. The right half of the ventral arch of the *atlas*. The distance between the outer edges of the articular surfaces is 36 mm, and must have been at least 37 mm in the perfectly intact bone. The corresponding distance in M. gigantea is 25 mm, in a more than middle-sized M. javanica 15 mm.

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[1] In the dimensions of the bones I compare the fossil species with Manis javanica, because morphologically it resembles this most closely among all existing species, and with M. gigantea, because this living species comes nearest to it in the size of the body.

4. The left processus articularis superior and some adjacent bone substance of one of the basal *caudal vertebrae*, and the adherent extremity of the processus articularis inferior of the preceding caudal vertebrae. The dimensions are almost $2^1/_2$ times the corresponding ones in the more than middle-sized Manis javanica.

5. The upper end of the right *ulna* (Pl. upper row, fourth figure). The olecranon to the distal edge of the cavitas sigmoidea major and minor; the processus coronoides is broken off. In this articular cavity is a large part of the trochlea and the capitulum of the humerus, somewhat dislocated to the inside. The epiphysis of the olecranon was not yet united with the body of the bone. The length from the beak to the top of the olecranon is 65 mm. The corresponding measure is 33 mm in M. gigantea, 22 mm in the large M. javanica, 20.5 mm in a middle-sized one. Through its length, which is considerable compared with its thickness, the olecranon resembles that of M. javanica very closely; it is only still greater than proportional to the size of the body estimated by the vertebrae. This process is relatively much shorter and broader in M. gigantea.

6. The right *radius*, without the proximal epiphysis. (Pl. upper row, third figure 1). This had got detached, being still separately ossified. Nor are the distal epiphysis and the diaphysis united together. The length is 103 mm, in M. gigantea 69 mm, in a middle-sized M. javanica 53 mm. The smallest (dorso-volar) breadth of the distal epiphysis is 29 mm, and the greatest (at right angles to it) 35 mm, in M. gigantea resp. 19 mm and 25 mm, in a middle-sized M. javanica resp. 11 mm and 13 mm, and in a small one (but also full-grown) 9 and 10 mm The smallest diameter of the collum is 13 mm, in M. gigantea 6.7 mm, and in a large M. javanica 4.5 mm.

7. The proximal extremity of the left *radius* (Pl., upper row, second figure). The epiphysis is slightly dislocated. Its smallest breadth (dorso-volar) is 19.3 mm, its greatest breadth (at right angles to the latter) 32.2 mm. In M. gigantea these measures are resp. 13.6 mm and 20 mm, in a middle-sized M. javanica 9 mm and 13 mm, in a small adult M. javanica 6.5 mm and 11 mm.

The total length of the radius (with the two epiphyses) may be estimated at about 115 mm. In the M. gigantea (also with epiphyses not yet joined by bone) it is 73 mm, in a middle-sized M. javanica 57 mm, and in the small adult 45.5 mm.

In relation to its length the bone is, compared with that of M. javanica, particularly thick and strong.

8. The *metacarpal bone* of the left *middle finger* (Pl., bottom row, fifth figure). Against the proximal articular surface a piece of the os capitatum. Length 37 mm, breadth in the middle 16.5 mm, in a large M. javanica resp. 15.5 and 5.5 mm. Accordingly the bone in the fossil species is thicker in relation to its length than that of the living species.

9 and *10*. The *metacarpal bone* of the right *middle finger*, connected with the somewhat defect *first phalanx* (Pl., bottom row, second figure).

11 and *12*. The connected *first* and *second phalanx* of the left *middle finger*. (Pl., bottom row, fourth figure). Length of the first phalanx in the middle of the side surfaces, on the medial side 15.5 mm, on the lateral side 16 mm. Thickness in the middle 22 mm. In the large M. javanica these measures are 8.5 mm, 8.7 mm, and 6 mm. Hence the fossil bone is relatively to its length much thicker. Measured in the same way the length of the second phalanx is on the medial side 22 mm, on the lateral-side 22.5 mm, the breadth at the base 21 mm. In the large M. javanica the corresponding measures are 9 mm, 9 mm, and 6.3 mm. Also this fossil bone is, therefore, thicker relatively to its length than that of M, javanica.

The second phalanx of a middle finger in the Indian Museum at Calcutta, ascribed originally (1880) by LYDEKKER to a Manis sindiensis, and considered later (1886) to belong to Macrotherium, and then again (1891) assigned to Chalicotherium, is, as regards length, measured as above, and as regards dorso-volar dimension of the trochlea, in good agreement with M. palaejavanica, but the throchlea is broader on the volar side, and the base differs greatly in form; the latter lacks the long dorsal point, and the very broad volar rim ending knobby on every side in the pliocene and the recent species of Java.

13. The third or *nail phalanx* of the left *middle finger* (Pl., bottom row, third figure). Of this cleft phalanx the ulnar point has broken off and has got lost, probably over a third part of the total length of the bone. Likewise the radial point is absent, which is broken off still about $1^1/_2$ cm nearer the base. The length of what remains is 53 mm, and that of the whole bone may be estimated at 80 mm by comparison with the homonymous bone of other species of Manis, especially M. javanica, which the fossil bone resembles most closely. The thickness, between the dorsal and the volar edge of the base, is 27 mm, the breadth at the base 17.5 mm. In M. gigantea the last three measures are: 53 mm, 18 mm, and 11.5 mm. In M. javanica I find mostly 26 mm (as maximum 27 mm), 8,5 mm, and 6.2 mm in more than middle-sized specimens. In the plistocene M. Lydekkeri of India (cave deposits in the Presidency of Madras)¹), only known through the homonymous bone, the length is 57 mm and the width 12.5 mm. The cleaving begins dorsally in M. palaejavanica at 17 mm distance from the transversely truncated base, i.e. about $^1/_5$ of the total length of the phalanx, in M. gigantea at 17 mm from the rounded base point, or about $^1/_3$ of the total length, in M.

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¹) Tijdschr. Kon. Ned. Aardrijksk. Genootschap, loc. cit. p. 1268. The characters mentioned here, and besides the pointed form of the volar process of the base, sharply distinguish the Indian plistocene species from the M. gigantea. It is certainly also different from M. palaejavanica; I was able to establish this in the Indian Museum at Calcutta, where this fossil is preserved.

Lydekkeri at 10 mm distance from the truncated base or little more than $^1/_6$ of the total length, and in M. javanica at 10.5 mm or $^2/_5$ of the total length. Apart from this more proximal cleaving in M. palaejavanica, there exists the closest similarity in the shape of this bone with M. javanica. Both species are distinguished by the possession of small bars of bone, bounding the volar entrances to the vascular furrows on both sides. On the fossil bone they are broken off, but surfaces of fracture clearly betray their former presence. Besides, only the existing M. javanica has the sharp, antler-like ramified vascular furrows on the side surfaces of the nail phalanges in common with M. palaejavanica.

14. The *metacarpal bone* of the right *fourth finger* (Pl., bottom row, last figure). Length 33.5 mm. Breadth in the middle 9.5 mm. In M. javanica length 14 mm, breadth in the middle 3 mm; the bone is, accordingly, much slenderer. In M. gigantea, on the other hand, the metacarpal IV is still relatively thicker than in M. palaejavanica, for the length is 17.5 mm and the breadth in the middle 6.5 mm.

15 and *16.* The *phalanx prima* and *phalanx secunda* of the right fourth finger connected in their natural mutual position (Pl., bottom row, sixth figure). The length of the first bone, in the middle of the radial side, is 15 mm, in the middle of the ulnar side 14 mm, the breadth at the base 17 mm. The length of the second bone is 15 mm on the radial side and 19 mm on the ulnar side, the breadth at the base 15 mm. Accordingly the capitulum of this phalanx points very obliquely to the middle finger, as it does in M. javanica, which proves, that also M. palaejavanica supported itself, in its walk, on the outside edge of the forefeet (hands), turning its fingers inwards.

In M. javanica both phalanges are much slenderer. The corresponding lengths are 6.3 mm, 6 mm and 6 mm, 7.4 mm, the corresponding breadths 5 mm and 4.7 mm. In M. gigantea the first phalanx is as short and thick as in the fossil species of Java, but the second somewhat less.

17, 18, 19, 20. The *metacarpal bone* and the *three phalanges* of the left *fourth finger* (Pl., bottom row, first figure). Somewhat dislocated from their natural mutual position; on the ulnar side of the capitulum of the metacarpal bone, a *sesamoid bone*. The nail phalanx, broken off at 45 mm length, was probably as a whole 65 mm long. As in M. javanica and M. gigantea, it is somewhat obliquely flattened sidelong. The base measures from the back side to the palm side 23.5 mm, transverse 12.5 mm. The radial half is slightly defect, probably as a consequence of a morbid process during life. For the rest this phalanx has many characters in common with the nail phalanx of the middle finger.

21. The medial half of the upper end of the right *femur* with almost the entire caput and the trochanter minor; the lateral half is broken off. (Pl., middle row, fifth figure). The epiphysis of the caput and that of the trochanter minor were not yet united by bone with the body of the femur. Length of the fragment 86 mm; diameter of the caput, measured from the front backward, 40 mm; in a middle-sized M. javanica 15.5 mm, in M. gigantea 28 mm. Thickness of the diaphysis, measured in the same way, 27 mm, in the other two species 9 mm and 18 mm. Distance from the top of the trochanter minor to the top of the caput 52 mm resp. 24 mm and 40 mm. In comparison with those two living species the thickness of the caput and of the diaphysis and also the length of the collum is about proportional to the body length estimated.

22. The upper half of the left *tibia.* (Pl., upper row, first figure). The epiphysis is not yet united together with the shaft. Length of the fragment 122 mm. The length of the whole tibia was probably about 245 mm. The antero-posterior dimension of the epiphyses from the tuberositas to the middle of the concavity on the back side, is about 44 mm; the transverse dimension 64 mm, and the circumference of the diaphysis, measured at the fragment as low as possible, about at the thinnest place of the tibia, is 73 mm. These three dimensions are in a middle-sized M. javanica 15 mm, 24 mm, and 25 mm; in the M. gigantea 26 mm, 43 mm, and 40 mm. The tibia of the last is apparently not entirely full-grown.

23. The left *calcaneus.* (Pl., middle row, first figure and Fig. 1 *Ca.* In this figure, accurate outlines of a photograph, four tarsal bones are placed in their natural position). The total length is 72 mm, that of the part behind the articular surface for the astragalus, i.e. the length of the collum and the tuberositas (the epiphysis of which is not united by bone), is 39 mm or 55 $^0/_0$ of the total length, the width of the collum at its narrowest is 15 mm, the height idem 25 mm. In a middle-sized M. javanica these measures are resp. 28 mm, 15 mm, 5 mm, and 9,5 mm; the posterior part occupies 53,6 $^0/_0$ of the total length.

In M. gigantea the measures are resp. 44 mm, 19 mm, 14 mm, and 19 mm; the posterior part occupies 43.2 $^0/_0$ of the total length. The form of the calcaneus of M. palaejavanica presents a striking resemblance to that of M. javanica; especially on the lower side it is to be seen that, as regards body size, both are equally long, narrow, and high. On the other hand the calcaneus of M. gigantea is short, and at the bottom in its front half, not narrow and angular, but broad and flatter. The processus (in man "spina") peronealis is relatively smaller than in M. javanica.

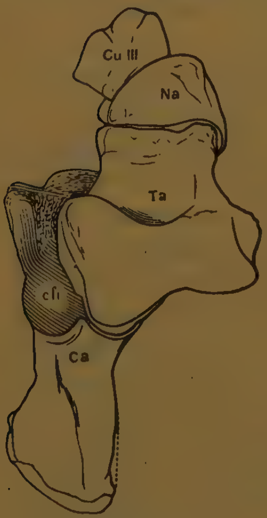

Fig. 1.
$^2/_3$ nat. size.

A very important difference between M. palaejavanica and M. javanica on one side, and M. gigantea on the other side, consists in this that the calcaneus of the two first-mentioned species does not articulate only with the astragalus but in a surface forming a lateral continuation of the articulating surface for the astragalus, the width of which is $^2/_3$ of that of the last-mentioned (fig. 1, the hatched part *c f i*), also with the lower border of the maleolus of the fibula, and chiefly with the back part of that lower border. This articular surface slopes down to the outside, that for the astragalus, with which it, however, forms a whole, to the inside. It is absent in the African species M. gigantea and M. temmincki Smuts, and also in the Asiatic M. pentadactyla L. en M. aurita Hodgs, but it *is* found in the African species M. tetradactyla L. and M. tricuspis Rafin. Through this particular articulation with the fibula the foot obtains the guidance and the firm support which it requires in its outwardly-turned (somewhat supine) position, especially when its claws, which in these particular species are distinguished by their large size, are active. All this — it also appears from other parts of the skeleton of the foot — applied undoubtedly also to the M. palaejavanica.

24. The left *talus* or astragalus (Pl., middle row, fourth figure and Fig. 1 *Ta*). The length measured normal to the tangent on the backside of the trochlea, is 44 mm, the greatest breadth is 42 mm. In a middle-sized M. javanica the length, measured in the same way, is 14.5 mm, in the M. gigantea 26 mm. The collum is relatively much narrower than in M. javanica, and does not point so obliquely inward. As in all Manidae, the caput is for the greater part concave, only near the inner edge convex to about the middle.

25. The left *navicular bone* (Pl., middle row, second figure. With the dislocated ectocuneiform bone, and Fig. 1, *Na*). Breadth, total 30 mm; in a middle-sized M. javanica 11 mm, and in the M. gigantea 19 mm. Length of the free dorsal surface 13 mm; in M. javanica 4,5 mm, in M. gigantea 8 mm.

26. The left *ectocuneiform bone* (Pl., middle row, second figure, and Fig. 1, *Cu III*). Breadth 22 mm. Length of the free dorsal surface 11 mm; in M. javanica 4.5 mm, in M. gigantea 6.5 mm. The anterior articular surface is, as in M. javanica, somewhat saddle-shaped, but on account of the strong outward turned, position of the articulating-surface with the navicular bone, turned also much more outward. The metatarsal of the middle toe and the toe itself was, however, not pointing much more outwards, as its base must have been very oblique to the axis of the bone, for the extant fourth metatarsal possesses such a very oblique basal plane.

27. The *metatarsal* of the right *second toe* (Fig. 2, *Mt II dext.* The outlines of these figures, too, are accurate photographic ones). Though this bone is slightly weathered at the surface, yet it is to be recognized with certainty as such, inter alia by the characteristic excavation of the base at the outside. The length measured in the direction of the axis,

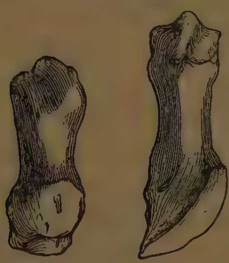

Fig. 2.
$^2/_3$ nat. size.

dorsally to the large plantar process of the base, is 38 mm, (the total length, with that plantar process, is 40.5 mm), the breadth of the diaphysis at its narrowest is 10.5 mm. In a middle-sized M. javanica the length is 16 mm and the breadth 3.2 mm.

28. The *metatarsal bone* of the left *fourth toe* (Pl. above the end of the top row, and Fig. 2, *Mt IV sin.*) The length, measured dorsally to the large plantar process of the base (here at the same time the greatest length), is 49 mm, the breadth of the diaphysis at its narrowest 10 mm; in a middle-sized M. javanica the length is 20,7 mm and the breadth 3,2 mm. The slightly convex basal articular surface is much *more obliquely turned outward* than in M. javanica, through which the base possesses a very sharp edge as outer rim, and the dorsal free surface presents a much acuter angle than ever occurs in M. javanica.

The *much more considerable length of the fourth* than of the second metatarsal bone the extinct giant pangolin of Java has in common only with M. javanica among all the existing Manis species. Except the existing Javanese pangolin all the recent species have these two metatarsalia of about the same length. This similarity in structure of the foot of the pliocene and of the living Manis of Java renders it already probable that also the pliocene Manis had large claws on its hind-feet as well as on its fore-feet, which implies similarity in the function of scratching open termite-hills or ant-dwellings. The outer border of the foot is turned somewhat downward, so that the animal throws the unearthed termites and ants under it, and not behind it. This resemblance in construction and function of the foot is corroborated by a peculiarity in the construction of the foot, which *distinguishes* M. palaejavanica from M. javanica. In the extinct giant pangolin the metatarsal of the fourth toe and also the metatarsal of the middle toe and the navicular bone were evidently at the same time particularly adapted to offer resistance to strong pressures exerted by the anterior part of the outer border of the foot — it is to be seen in the articular surfaces — in contrast with the homonymous bones of M. javanica. It may be inferred from this that by turning both the hind claws and the fore-claws under its feet, M. palaejavanica walked permanently on the outside also of its hind-feet, not only "sometimes", as is stated of M. javanica¹). But this permanent mode of walking is, at the same time, a sure indication of the possession of large claws also on the hind-feet.

It may, therefore, be assumed that in both species the two pairs of extremities were less specialized than in the other Manidae; moreover the recent species of Java lives chiefly on the ground, but it does also climb. For climbing the extinct giant pangolin will undoubtedly have been too heavy, certainly even more so than the existing African M. gigantea.

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¹) By W. T. BLANFORD, according to Tickell, in "The Fauna of British India. Mammalia", p. 600. London 1891.

Although constituting a true (natural) genus, the existing Manidae are devided into two tribes, further they are differently specialized.

Of the four existing African species, which as appears from the common possession of certain distinguishing characters (as the form of the xiphisternum and the arrangement of the scales on the tail) certainly belong to one tribe, whereas the three Asiatic species classified according to these peculiarities, form another tribe, two species are adapted exclusively to a life on the ground, through specialisation of their fore- and hind limbs. They find their food on the ground: termites and ants, chiefly termites, and the hills of these latter mostly reaching considerable heights in Africa, the closely allied M. temmincki Smuts and Manis gigantea Ill. have assumed to a certain extent bipede locomotion. The first-mentioned species, which inhabits the steppes and savannas of South Africa, north of the Vaal-river, and East-Africa to 17° N.L., even walks almost exclusively on its hind-legs, the heavy, broad tail being used not as a support, but to keep its balance. As in the plantigrade mammals their hind feet are provided with toes and claws differing comparatively little in size inter se, whereas on the fore-feet the three middle ones, especially the middle toe and claw, have grown to gigantic dimensions. Standing on their hind feet more or less erect, they use there fore-fect like pickaxes to scratch, or rather hew, open very hard termite-hills, often some meters high. Also M. temmincki is of considerable size, and can therefore reach high with its fore-claws.

The two other African species: M. tricuspis Rafin. and M. tetradactyla L. (M. longicaudata Briss), which, with M. gigantea, inhabit West Africa between the Gambia and the Kunene, are small, possess a long prehensile tail, which in its functions exceeds the tail of M. javanica no less than the admirably perfect prehensile tail of Ateles that of Mycetes, and live chiefly in the trees, where they, being excellent climbers, seek termites (which build there round nests, the size of a mans head, on the branches out of their own excrements) and ants. They have long middle toes, both on the hind- and on the fore-feet, but since they do not, or only rarely, use their hind feet to scratch open termite- or antnests on the ground, their fourth metatarsal is not longer, or longer only in an insignificant degree than the second. Their calcaneus, however, does resemble that of M. javanica somewhat.

Of the three existing Asiatic species, M. javanica, which inhabits besides the Great Sunda Islands, also the continental area east from the Bay of Bengal and south from the habitat of M. aurita, has not to do with very high termite hills; those in Java, at least, are hardly higher than a meter. This species chiefly lives on the ground, and does not climb very nimbly. The fore-feet and the hind-feet, both provided with large claws, are used for scratching open the low termite-hills and ant-dwellings, which moreover are not so very hard. M. pentadactyla L. of India and Ceylon, and M. aurita Hodgs of Nepal, Assam and South China, Hainan and

Formosa, have, on the other hand, again to deal with high termite hills; as far as I have been able to ascertain they climb seldomer than M. javanica, live more exclusively on the ground. The three middle claws of their hind feet have scarcely half the length of those of the fore-feet [1]). It is known at least of M. pentadactyla that it habitually stands on its hind-feet. They have their extremities already more specialized than M. javanica and M. palaejavanica. Accordingly these two species are really to be considered as the least specialized of all the Manidae known. This finds a striking confirmation in the fact that the cephalisation of M. javanica is only as high (the volume of the brain calculated for the same body weight, half as great) as that of M. gigantea and M. tetradactyla. Wanting data on the body weight, I had no opportunity to examine the cephalisation of M. temmincki and M. tricuspis properly, nor of M. pentadactyla and M. aurita; apparently the two first-mentioned may be considered equal to the two other African species of which I was able to calculate the cephalisation of specimens in the Rijks-Museum van Natuurlijke Historie at Leyden. Among the Asiatic species, M. pentadactyla and M. aurita on the other hand, do not rise above M. javanica, judging from the few available data.

The species arose by adaptation to the different particular conditions of life, imposed on the animal by the world in which it had to live, especially with regard to the regional character of the termite nests, which contain their principal food, and the circumstances of life in the original home of the Asiatic tribe of the genus must actually have differed little from those which exist to-day in the habitat of M. javanica.

Probably these were more favourable to that tribe in the Pliocene time than they are at present, and this time coincides with its flourishing period in that region, as may be deduced from the occurrence of the giant form. As all the Manis species live in open and comparatively dry regions, it may be assured, that the then climate of what is now Java, was still somewhat drier. This corroborates what was already to be inferred from the continental character of the Kendeng-fauna as a whole, viz. that Java at the time of its existence constituted a part of the Asiatic continent, and formed, with the other Great Sunda Islands an appendage to the present continental area east from the Bay of Bengal, of which geographical condition a climate less humid than at present was a necessary consequence.

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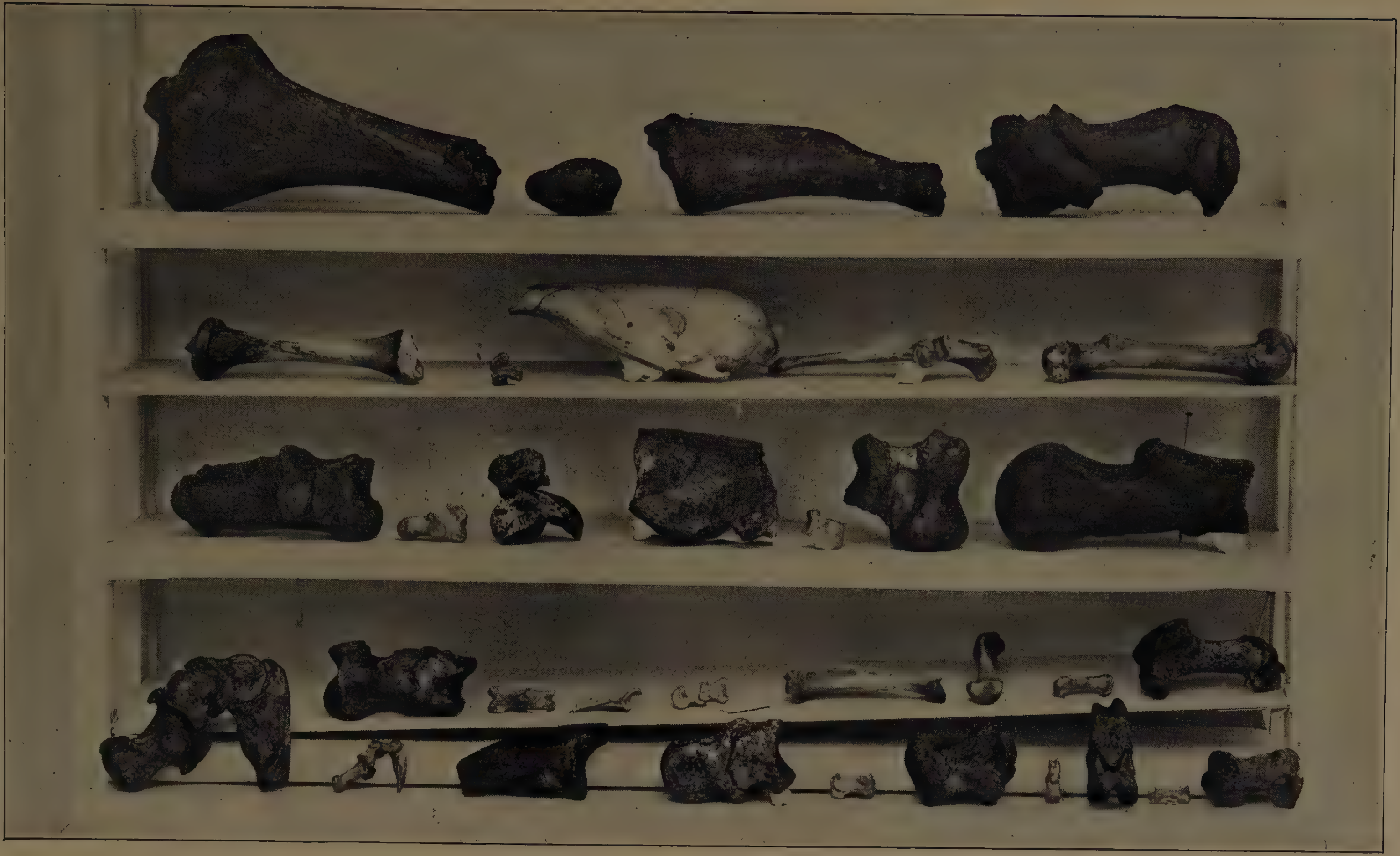
[1]) The significance of the relative length of the fore- and hind claws for the systematization of the Manidae had already been realized by F. A. JENTINK („Revision of the Manidae in the Leyden Museum". Notes from the Leyden Museum. Vol. IV, p. 193—209. 1882) and P. MATSCHIE („Die natürliche Verwandtschaft und die Verbreitung der Manis-Arten". Sitzungs-Berichte der Gesellschaft naturforschender Freunde zu Berlin, Jahrgang 1894, p. 1—11).

EUG. DUBOIS: "MANIS PALAEJAVANICA, THE GIGANTIC PANGOLIN OF THE KENDENG-FAUNA".



Manis palaejavanica Dubois and *Manis javanica* Desm. (Somewhat more than $^{2}/_{5}$ nat. size).

EXPLANATION OF THE PLATE.

Photographic figures of 24 (of the 28 collected) bones of *Manis palaejavanica* and the homonymous bones of *Manis javanica*, mostly near each other; the radii of the former species, however, lie in the upper row, of the latter in the lower row. Partly the bones were found connected in their natural mutual position, some slightly, the ectocuneiform bone considerably, dislocated. The corresponding bones of *Manis javanica* are connected with each other in the same way as in the fossil bones found.

Chemistry.— *"On Lyotropy."* By H. R. KRUYT and CONMAR ROBINSON.

(Communicated at the meeting of April 24, 1926) [1]).

The behaviour of electrolytes in solution is only partially explained by the osmotic theory. There are several properties of solutions of electrolytes which cannot be connected with the number of particles in solution. These properties are found for instance where one investigates the influence of electrolytes on the solubility of non-electrolytes, on reaction velocities, on the salting out of proteins, on the swelling of gels, on the surface tension of water and on the maximum density of water. In all these cases the effect of equimolecular solution is not the same and the influence which the salt exerts is a function of both the cation and the anion. The ions can be arranged in a series which gives the order in which they exert their influence.

A phenomenon not yet mentioned that shows this series is the electric mobility of the ions, which for the alkali metals is just in the reverse order to what we might expect from the size of the atoms. For a long time this has been accounted for by the property of the ions of binding water molecules. The sequence of the lyotropic series will therefore be that of the hydration of the ions. While not denying the truth of this explanation, it is certainly not complete ; it can, however, suffice to explain most of the above mentioned phenomena. But to explain, for example, the influence of electrolytes on the surface tension of water one is inclined to turn to the influence of these substances or the molecular aggregation of the water.

Seeing that lyotropy plays so important a part in colloid chemistry, we have set out to investigate those phenomena which can be most easily controled. We first of all wished to show that LOEB's [2]) explanation that the lyotropic series is simply a consequence of alterations in the hydrogen ion concentration is wrong. For this purpose we investigated the influence of the addition of chlorides on the limited miscibility of phenol and water.

As in the meantime DUCKET and PATTERSON [3]) published a similar research, we shall not here quote our results except to say that they showed that KCl and HCl have exactly the same influence, which in itself is a complete refutation of LOEB's theory when extended to cover substances others than proteins.

Subsequently we investigated the solubility influence. We found that systematic data were only available for one substance, namely phenylthiourea [1]). In recent literature there is a very interesting investigation by LINDESTRÖM-LANG [2]) which prompted us to extend this research in order to establish for certainty certain conclusions which one is inclined to come to when considering his experiments. From his results combined with ours, one is able to draw the following noteworthy conclusions. The influence of salts on the solubility of quinone is only dependent on their anions. With what cation the anion is combined is almost immaterial. With hydroquinone the facts are just the reverse. Here one has a cation lyotropy while the anion plays a very subordinate role. In tables 1 and 2 are given the results of our experiments; those marked with a * are taken from the work of LINDESTRÖM-LANG (interpolated from 1.5m). In the third column in these tables the solubility in water is given as equal to 100; as the solubility in water in our experiments was not exactly the same as in the experiments of LINDESTRÖM-LANG, we only brought these relative numbers into our tables. In fig. 1 and 2 the results are shown graphically, from which one may see directly the typical anion lyotropy for quinone and the cation lyotropy of hydroquinone.

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[1]) Published in this Academy's "Verslag der gewone vergaderingen", Vol. 35, p. 812, (meeting of September 25, 1926).

[2]) J. LOEB, Proteins and the Theory of colloidal Behavior, New-York 1922.

[3]) J. DUCKET and W. H. PATTERSON, J. physic. chem. 29, 295 (1925).

From LINDESTRÖM-LANG's research it seems that succinic acid and boric acid belong to the hydroquinone type. We have tried to find other substances which belong to the quinone type. Firstly we chose substances which should have a more or less basic character, since the acids mentioned above belong to the type exhibiting cation lyotropy. In tables 3 and 4 are given the figures for meta and para nitroaniline respectively, in table 5 those for para phenylenediamine. In fig. 3 are given the results for salt additions of 0.2 m.

The analysis of the saturated solutions in the case of the nitroanilines was carried out by a specially developed method (potentiometric titration with $TiCl_3$) which has already been published elsewhere [3]). The solubility of the diamines was determined by precipitation of the diamine with picric acid, filtering off the picrate and back titrating with baryta using methyl red as indicator.

From the figure one sees directly that in all these three cases we have to do with anion lyotropy, exactly as in the case with quinone; there is a great influence of anions and a very limited influence of cations [4]).

Finally in table 6 are given the results with nitrophenol (see also fig. 3). This gives the impression that here we are dealing with an intermediate case, as the influence of both anions and cations are quite marked.

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[1]) V. ROTHMUND, Z. physik. Chem. 33, 401 (1900); W. BILTZ, ibidem 43, 41 (1903).

[2]) K. LINDESTRÖM-LANG, C. r. Lab. Carlsberg 15, Nr. 4 (1924).

[3]) I. M. KOLTHOFF et C. ROBINSON, Rec. Trav. Chim. 46, 169 (1926).

[4]) With phenylenediamine we have a reversal of the series K—Na—Li. We cannot say with certainty how this should be interpreted. There are other cases where Li is found out of its place (cf. V. ROTHMUND, Löslichkeit und Löslichkeitsbeeinflüssung p. 153, Leipzig 1906).

TABLE 1.

Quinone — Temperature: 23.75°

Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	13.97	100.0
1.5 m KSCN	23.77	170.1
„ KI	20.89	149.6
„ KNO_3	18.46	132.1
„ KBr	15.15	108.5
„ KCl	12.63	90.4
„ K_2SO_4	8.90	63.7
„ *LiCl	—	77.3
„ *NaCl	—	80.3
„ *RbCl	—	93.8 (18°)
„ CsCl	—	97.6 (18°)

TABLE 2.

Hydroquinone — Temperature: 23.75°

Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	67.64	100.0
1.5 m KI	50.62	74.8
„ KNO_3	54.09	80.0
„ KBr	47.91	70.8
„ *KCl	—	67.0
$^1/_2$ m K_2SO_4 [1]	52.72	$(^1/_2\ m) = 78.0$ of $\left(\frac{1.5\ m}{2}\right) = 68$
1.5 m *LiCl	—	56.6
„ *NaCl	—	59.1
„ *CsCl	—	95.0

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[1] On account of incomplete solution of the salt, only one determination with $^1/_2$ m. K_2SO_4 was made. This gave a solubility for hydroquinone of 52,72 grams per litre or 78 $^0/_0$. This gives by linear extrapolation a value of 68 $^0/_0$ for $\frac{1.5}{2}$ m. K_2SO_4.

TABLE 3.

m-Nitroaniline — Temperature 25°

Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	0.8929	100.0
0.2 m KI	0.9527	106.7
„ KBr	0.8857	99.2
„ KCl	0.8619	96.5
$\frac{0.2\ \text{m}}{2}$ K_2SO_4	0.8349	93.5
0.2 m LiCl	0.8449	94.6
„ NaCl	0.8514	95.3

TABLE 4.

p-Nitroaniline — Temperature 25°

Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	0.5735	100.0
0.2 m KI	0.6053	105.5
„ KBr	0.5834	101.7
„ KCl	0.5606	97.7
$\frac{0.2\ \text{m}}{2}$ K_2SO_4	0.5430	94.7
0.2 m LiCl	0.5430	94.7
„ NaCl	0.5480	95.5

TABLE 5.

p-Phenylenediamine — Temperature 25°

Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	47.23	100.0
0.2 m KI	51.68	109.4
„ KBr	48.68	103.0
„ KCl	46.85	99.2
$\frac{0.2\ \text{m}}{2}$ K_2SO_4	43.21	91.5
0.2 m LiCl	48.32	102.3
„ NaCl	47.23	100.0

TABLE 6.

p.-Nitrophenol — Temperature 25°

Added electrolyte	Solubility in grams per litre	Solubility as percentage of that in water
Water	11.82	100.0
0.2 m KI	12.45	105.3
„ KBr	11.91	100.8
„ KCl	11.55	97.7
$\frac{0.2\ m}{2}$ K_2SO_4	11.50	97.3
0.2 m LiCl	10.90	92.2
„ NaCl	11.05	93.5

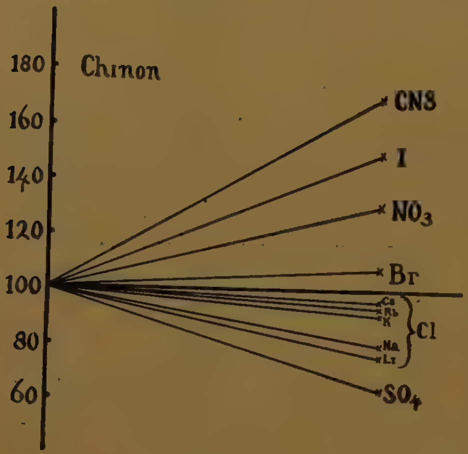

Fig. 1.

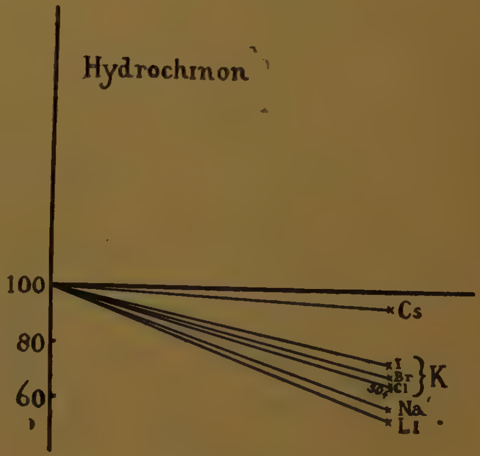

Fig. 2.

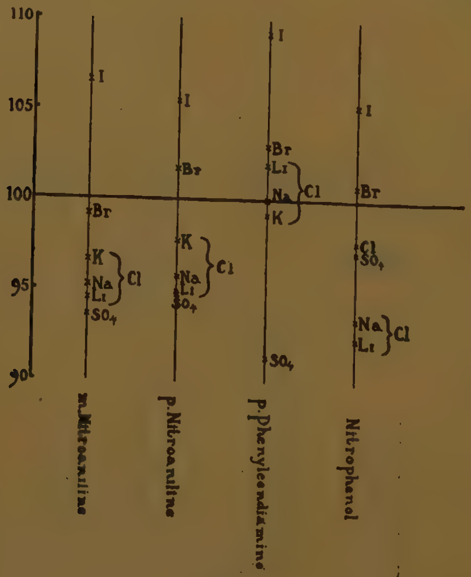

Fig. 3.

The investigations described above are of interest in the understanding of lyotropy. Thus while one usually bases theories of lyotropy on the "neutral salt influence" and the „salting out effect", here we have a marked specific influence of both cation and anion and also the frequent occurrence of an increase of solubility by the added salt.

DEBIJE [1]) has recently connected the lowering of the solubility of organic substances by addition of electrolytes with the fact that these organic substances lower the dielectric constant of water. Increase of solubility is not so easily accounted for by this theory and it does not lead us to expect a specific influence of the ions. It seems to us that an explanation may more easily be found in the orientation of the dipoles of the water in the immediate neighbourhood of the ions, that is to say the orientation of the water of hydration, although at present one can only make surmises.

We have already stated that various physico-chemical phenomena show that hydration decrease in the following order:

$$\text{cations}: \quad \mathrm{Li} > \mathrm{Na} > \mathrm{K} > \mathrm{Rb} > \mathrm{Cs}$$
$$\text{anions}: \quad \mathrm{SO_4} > \mathrm{Cl} > \mathrm{Br} > \mathrm{NO_3} > \mathrm{J} > \mathrm{CNS}$$

This in general will be the sequence for the salting out effect, Li and SO_4 having a strong, and Cs and CNS a weak salting out effect. Hence we always find this series.

The solution of a substance implies an attractive force between the molecules of the substance and those of the solvent. As we may consider this attraction electrical in origin, the water molecules will not only be attracted, but in consequence of their dipolar character they will be orientated. Two kinds of orientation are of course possible: either the positive end or the negative end of the water molecule may be turned towards the solute molecules. Assuming a polar character of the dissolved organic substance, one of these two orientations must preponderate. At the same time however there will be an attraction for one of the ions of the dissolved salt. But also there will be orientated water molecules round these ions.

Now if for example the molecule is anionphilic (we assume that quinone and the amines investigated belong to this class) then the orientation of the dipoles round the anions will favour the orientation round the organic molecules and hence increase their solubility. Cations on the other hand will bring about a decrease in the solubility but their influence will be small since their concentration will be less in the neighbourhood of the organic molecules.

Thus, as well as the ordinary salting out effect there is an increase of solubility brought about (in this case) by the anions. The CNS lowers the solubility very little on account of its low hydration and the increase in solubility will therefore preponderate. The sulphate ion has a strong lowering influence and its lowering influence will therefore preponderate. The influence of the cations is quite subordinate since they are kept further from the molecule. What small influence they do exert will be in the order of their salting out effect. In fact here we have the behaviour of quinone and the nitroanilines investigated. For cationphilic substances (hydroquinone and the acids) an exactly corresponding argument holds.

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[1]) P. DEBIJE, Physik. Z. 26, 22 (1925).

Seeing the present hypothetical character of these considerations we are at present further developing the theory. We hope later to return to the subject when we will publish our investigations on colloidal systems.

VAN 'T HOFF *Laboratory.*

Utrecht, April 1926.

Mathematics. — *"Ueber stetige Kurven."* By JULIA RÓŻAŃSKA. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of May 29, 1926).

Das Ziel dieser Arbeit ist, ausgehend von einigen Eigenschaften einer stetigen Kurve „im kleinen", d.h. in der Umgebung irgend eines ihrer Punkte, auf den Verlauf der Kurve „im grossen" zu schliessen.

Anknüpfend an die Arbeiten von PAUL URYSOHN über die Cantorschen Kurven, deren im Folgenden verwendeten Resultate sich auch bei K. MENGER befinden, 1) gebe ich die Definition vom Integralindex für die Punkte einer beliebigen Cantorschen Kurve. 2) Die Vergleichung des URYSOHN-MENGER'schen Verzweigungsindex mit dem Integralindex gestattet mir eine neue lokal-integrale Charakteristik der sogenannten „Baumkurven", sowie die notwendigen und hinreichenden Bedingungen dafür zu geben, dass eine stetige Kurve eine und nur eine einfache geschlossene Linie enthält.

Herrn PAUL ALEXANDROFF, der mich auf die Unabhängigkeit dieser Resultate von der Topologie der Ebene aufmerksam gemacht und viele wertvolle Ratschläge bezüglich der Redaktion dieser Arbeit gegeben hat, spreche ich an dieser Stelle meinen Dank aus.

Definition des Integralindex.

Es sei C eine Cantorsche Kurve, x ein Punkt von C.

1. x ist vom Integralindex m (wobei m eine natürliche Zahl, $\aleph_0$ oder $\mathfrak{c}$ ist) falls m die kleinste so beschaffene Kardinalzahl ist, dass es für jedes $\varepsilon > 0$ eine ε-Aussonderung $C = A + B + D$ 3) gibt, von der Art, dass die abgeschlossene Menge D aus m Komponenten besteht.

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1) URYSOHN, Comptes Rendus t. 175 (1922), p. 440, 481; *„Mémoire sur les multiplicités Cantoriennes"*, II. Teil (erscheint demnächst in den Verhandelingen der Kgl. Akademie der Wissenschaften zu Amsterdam; diese Arbeit wird in folgendem einfach als URYSOHN, II zitiert); K. MENGER, *„Grundzüge einer Theorie der Kurven"*, Proceed. Ak. Amsterdam, XXVIII, SS. 67-71 und Math. Annalen, 95, SS. 277-306.

2) Ein Hinweis in dieser Richtung findet sich bei MENGER, Math. Ann. 95, S. 281, Fussnote 8).

3) Die Zerlegung $C = A + B + D$ in zueinander fremde Mengen heisst nach URYSOHN eine ε-Aussonderung von x auf C wenn

$$x \subset A \subset A + B \subset S(x, \varepsilon) \quad \ldots \ldots \quad (1)$$

$$A \,.\, \overline{D} + \overline{A} \,.\, D = O \quad \ldots \ldots \quad (2)$$

Die Menge B wird im Folgenden stets eine abgeschlossene nulldimensionale (also in C nirgends dichte) Menge sein. Vgl. wegen der Terminologie URYSOHN, Mémoire mult. cant., I, Introduction (§§ 15—21, Fund. Math., VII, SS. 49—64).

2. x ist vom Integralindex ω, wenn für jedes $\varepsilon > 0$ eine ε-Aussonderung $C = A + B + D$ vorhanden ist von der Art, dass $\overline{D}$ aus endlich vielen Komponenten besteht, wobei die Anzahl dieser Komponenten mit $\frac{1}{\varepsilon}$ notwendig gegen ∞ strebt.

Es wird (wie in der Verzweigungstheorie) die Verabredung getroffen

$$n < \omega < \aleph_0 < \mathfrak{c}.$$

Bemerkung 1. Die Aussonderungsmengen B, die zum gegebenen ε die Minimaleigenschaft in bezug auf die Komponentenanzahl der Menge $\overline{D}$ besitzen, brauchen nicht notwendig eine, der Indexdefinition entsprechende Mächtigkeit zu haben. Doch werden wir später sehen, dass wir stets im Falle der stetigen Kurven die betreffenden Aussonderungsmengen gebrauchen können.

Es gilt aber ohne weiteres der:

Satz I. *Für jeden Punkt x der Kurve C ist $\mathit{Ind}_x\, C \leqq \mathit{ind}_x\, C$.*

Um diesen Satz zu beweisen, genügt es zu zeigen, dass jede Komponente K der Menge $\overline{D}$ (wo $C = A + B + D$ eine beliebige ε-Aussonderung des Punktes x ist) mit B wenigstens einen Punkt gemeinsam hat. Falls nun letztere Behauptung falsch wäre, würden die beiden Mengen $B . \overline{D}$ und K zueinander fremd sein; da aber K eine *Komponente* von $\overline{D}$ ist, so folgt daraus die Existenz einer Zerlegung

$$\overline{D} = F_1 + F_2 \tag{1}$$

in zwei zueinander fremde, den Bedingungen $F_1 \supset B . \overline{D}$, $F_2 \supset K$ genügende abgeschlossene Mengen. Die Zerlegung (1) hat aber die widerspruchsvolle Zerlegung $C = (A + B + F_1) + F_2$ des Kontinuums C in zwei zueinander fremde abgeschlossene Mengen $A + B + F_1$ und F_2 zur Folge. Der Satz I ist hiermit bewiesen.

Bemerkung 2. Wir können stets annehmen, dass jeder Punkt y von B gleichzeitig Häufungspunkt der beiden Mengen A und D ist. In der Tat ist jeder Punkt y von B ein Häufungspunkt mindestens einer der beiden Mengen A und D; denn andernfalls wäre C kein Kontinuum [1]. Alle Punkte y, die nur einer der Mengen $\overline{A}$ bzw. $\overline{D}$ angehören, fügen wir zu den entsprechenden Mengen A bzw. D hinzu, ohne dass $B^* = B - \{y\}$ ihre Eigenschaften als Aussonderungsmenge verliert. Ausserdem ist B^* wieder abgeschlossen; denn jeder Häufungspunkt von B^* gehört gleichzeitig zu den abgeschlossenen Mengen B, $\overline{A}$ und $\overline{D}$.

Nur solche Aussonderungsmengen werden wir von hier an betrachten. Also haben wir immer:

$$\overline{D} = D + B \qquad \overline{A} = A + B\ ^{2)}.$$

---

[1] Die Menge B war ja als nulldimensionale abgeschlossene Menge vorausgesetzt.

[2] Diese Bedingung hat wie leicht ersichtlich keinen Einfluss auf die Bestimmung von $\mathit{ind}_x\, C$ und $\mathit{Ind}_x\, C$.

Wir wenden uns jetzt zu den stetigen, d. h. im kleinen zusammenhängenden[1]) Kurven C.

Satz II. *Für jeden Punkt x einer stetigen Kurve C ist $\mathrm{Ind}_x\, C \leqq \omega$.*

Der Beweis des Satzes stützt sich auf den folgenden

Hilfssatz: *Es sei $C = A + B + D$ eine ε-Aussonderung des Punktes x der stetigen Kurve C. Dann enthält $\overline{D}$ nur eine endliche Anzahl von Komponenten, deren Durchmesser eine vorgegebene positive Grösse α übertrifft.*

Beweis. Nehmen wir im Gegenteil an, es existiere eine Zahl $\alpha > 0$, so dass $\overline{D}$ unendlich viele Komponenten K mit $\delta(K) > \alpha$ enthält.

Infolge eines bekannten Satzes[2]) ist es möglich eine (im Sinne von HAUSDORFF) konvergente Folge aus $\{K\}$ zu wählen. Es sei $K_1, K_2, \dots K_n, \dots$ eine solche Folge und $lt\,(K_i) = K^*$ ihr topologischer Limes. K^* ist ein Kontinuum. Dann ist:

$1^0.\ \delta(K^*) \geqq \alpha$; $2^0.\ K^* \subset \overline{D}$; $3^0.\ K_i \,.\, K^* = 0$ (mit Ausnahme vielleicht einer einzigen Komponente, die dann K^* enthält und die wir in Folgendem vernachlässigen können).

Da B eine nulldimensionale abgeschlossene Menge ist, ist die abgeschlossene Menge $B \,.\, K^*$ auf dem *Kontinuum* K^* nirgends dicht. Es gibt also einen Punkt $y \subset K^*$ mit $\varrho\,(y, B) \geqq \eta > 0$. Es sei $\delta > 0$ beliebig gegeben. Infolge der Definition des topologischen Limes ist es möglich einen Punkt $z \subset K_r$ (bei genügend grossem r) zu finden von der Art, dass $\varrho\,(y, z) < \delta$ ist.

Es sei nun Q irgendein, die beiden Punkte y und z verbindendes Teilkontinuum von C. Wir wollen zeigen, dass $Q \,.\, B \neq 0$ ist. In der Tat, falls $Q \,.\, B = 0$ wäre, so würde Q (da es $y + z$ enthält) in $C - A = \overline{D}$ enthalten sein. Da aber $z \subset K_r$ ist, so wäre auch $Q \subset K_r$, und also $K_r \,.\, K^* \supset Q \,.\, K^* \supset z \neq 0$, was der Bedingung 2^0. widerspricht. Aus der soeben bewiesenen Relation $Q \,.\, B \neq 0$ folgt, dass $\delta\,(Q) \geqq \eta$ ist; da aber δ und Q beliebig gewählt waren, so heisst dies, dass

$$\varrho_c\,(y, z) \geqq \varrho\,(y, B) \geqq \eta \quad \text{ist.}$$

Also ist der Punkt y kein Stetigkeitspunkt der Kurve. Der Hilfssatz ist bewiesen.

Aus diesem Hilfssatz folgt unsre Annahme, dass die Menge der Komponenten von $\overline{D}$ bei jeder ε-Aussonderung der stetigen Kurve C höchstens abzählbar ist.

Es sei jetzt ε_1 eine beliebige positive Zahl und $C = A_1 + B_1 + D_1$

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[1]) Der Begriff des "Zusammenhanges im kleinen" (Stetigheit) wurde zuerst von HAHN eingeführt, unabhängig auch von MASURKIEWICZ behandelt und lautet folgendermassen: die Kurve C heisst "zusammenhängend im kleinen" (stetig) im Punkte x, wenn es für jedes ε eine Zahl δ gibt von der Art, dass für zwei Punkte x und y, deren Abstand $\rho\,(x, y) < \delta$ ist, der relative Abstand $\rho_c\,(x, y) < \varepsilon$ ist, wobei $\rho_c\,(x, y)$ die untere Grenze der Durchmesser aller Teilkontinua von C, die x und y gleichzeitig enthalten, bedeutet.

[2]) URYSOHN, II, Ch. II. VIETORIS, Stetige Mengen (Monatsh. f. Math. u. Phys., 1921).

irgendeine ε_1-Aussonderung des Punktes x. Wir bezeichnen dann durch δ die positive Zahl $\varrho(x, B_1 + D_1)$ (es ist stets $0 < \delta < \varepsilon_1$).

Wir setzen nun $\varepsilon_2 = \frac{\delta}{2}$ und betrachten irgend eine ε_0-Aussonderung des Punktes x

$$C = A_2 + B_2 + D_2, \qquad x \subset A_2 \subset A_2 + B_2 \subset S(x, \varepsilon_2) = S\left(x, \frac{\delta}{2}\right).$$

Es seien jetzt $\{K\}$ bzw. $\{K^*\}$ die Komponenten von $\overline{D}_1$ bzw. $\overline{D}_2$. Die Menge $\overline{D}_1 = D_1 + B_1$ (und folglich jede Komponente K) ist dann zu $S(x, \delta)$ fremd. Jede Komponente K^* hat notwendig Punkte mit $S\left(x, \frac{\delta}{2}\right)$ gemeinsam, nämlich die Punkte von $B_2 \,.\, K^* \neq 0$.

Es ist ausserdem $A_2 \subset A_1$ und folglich $\overline{D}_2 \supset \overline{D}_1$. Jede Komponente K ist in einer Komponente K^* enthalten. Es gibt aber nur eine endliche Anzahl von Komponenten K^*, die mindestens ein K enthalten, weil Komponenten K^*, da sie gleichzeitig Punkte ausserhalb $S(x, \delta)$ und innerhalb $S\left(x, \frac{\delta}{2}\right)$ enthalten müssen, sämtlich einen Durchmesser grösser als $\frac{\delta}{2}$ haben. Also kann ihre Anzahl dem Hilfssatz gemäss unmöglich unendlich sein.

Es seien nun $K_1^*, K_2^* \ldots K_m^*$ diese Komponenten. Es ist

$$D_2 = \Sigma\, K^* = \sum_1^m K_i^* + \sum_{K^* \subset A_1} K^*$$ 1),

und

$$B_2 = B_2 \,.\, \overline{D}_2 = B_2 \,.\, \sum_1^m K_i^* + B_2 \,.\, \sum_{K^* \subset A_1} K^* = B_1^* + B_2 \,.\, \sum_{K^* \subset A_1} K^* .$$

Die Identität $C = A_1^* + B_1^* + D_1^*$, wobei

$$B_1^* = B_2 \,.\, \sum_1^m K_i^*$$

$$A_1^* = A_2 + \sum_{K^* \subset A_1} K^*$$

$$D_1^* = \sum_1^m K_i^* - (B_1^* + A_1^*)$$

gesetzt ist 2), gibt uns eine ε_1-Aussonderung des Punktes x.

---

1) Letztere Summe bezieht sich auf alle diejenigen K^* die zu $\overline{D}_1$ fremd, und also in A enthalten sind.

2) Man bemerkt sofort, dass $D_1^* = \sum_1^m K_1^* - B_1^*$ ist.

In der Tat haben wir:

1) $A_1^* \supset A_2 \supset x$; 2) $A_1^* + B_1^* \subset A_2 + B_2 + \sum\limits_{K^* \subset A_1} K^* \subset S(x, \varepsilon_1)$;

$$3)\quad A_1^* \,.\, \overline{D_1^*} + \overline{A_1^*} \,.\, D_1^* \subset \Big(A_2 + \sum_{K^* \subset A_1} K^*\Big) \,.\, \sum_1^m K_i^* + \overline{A_2} \,.\, \Big(\sum_1^m K_i^* - B_1^*\Big) +$$

$$+ \overline{\sum_{K^* \subset A_1} K^*} \,.\, \Big(\sum_1^m K_i^* - B_1^*\Big).$$

Aus unsern Definitionen folgt leicht, dass der erste und zweite Summand von (3) leer ist. Es bleibt also zu beweisen, dass $\overline{\sum\limits_{K^* \subset A_1} K^*} \,.\, (\sum\limits_1^m K_i^* - B_1^*) = 0$ ist. Der zweite Faktor enthält weder Punkte von B_2, noch von $\sum\limits_{K^* \subset A_1} K^*$; die gemeinsamen Punkte der beiden Faktoren könnten also nur diejenigen Häufungspunkte von $\sum\limits_{K^* \subset A_1} K^*$ sein, die weder zu $\sum\limits_{K^* \subset A_1} K^*$, noch zu B_2 gehören. Solche existieren aber überhaupt nicht. In der Tat streben die Durchmesser der in A enthaltenen K^* dem Hilfssatz gemäss gegen Null, d.h. dass jede konvergente unendliche Folge von Komponenten $K^* \subset A_1$ gegen einen Punkt konvergiert. Da aber jede Komponente notwendig einen Punkt auf der abgeschlossenen Menge B_2 besitzt, gehört dieser Limespunkt auch zu B_2.

Wir sehen jetzt, dass die Zerlegung $C = A_1^* + B_1^* + D_1^*$ wirklich eine ε_1-Aussonderung des Punktes x ist. Die Menge $\overline{D_1^*}$ besteht dabei aus einer endlichen Anzahl von Komponenten. Da ε_1 aber eine beliebige positive Zahl war, so heisst das, dass $Ind_x\, C \leqq \omega$ ist, w. z. b. w.[1])

Wir wollen nun den Integralindex mit dem Verzweigungsindex etwas näher vergleichen.

Satz III. *Bei der Bestimmung des Integralindex der stetigen Kurve C können wir uns auf die Aussonderungsmengen B von minimaler d.h. der, dem Indexe des betreffenden Punktes entsprechenden, Mächtigkeit beschränken.* [2])

Beweis. Es seien $\varepsilon > 0$ und eine ε-Aussonderung $C = A + B + D$ des Punktes x gegeben, wobei die Mächtigkeit der Komponentenmenge von $\overline{D} = \sum\limits_1^m K_i$ den kleinstmöglichen Wert annimmt. Wir wollen zeigen, dass es stets eine ε-aussondernde abgeschlossene Menge B_1 von minimaler Mächtigkeit gibt, die in bezug auf die Komponentenanzahl von $\overline{D_1}$ die Eigenschaften von B besitzt. In der Tat gibt es nach der Definition des Verzweigungsindex eine den Punkt x ε-aussondernde, in A enthaltene

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[1]) Aus diesem Satz folgt insbesondere, dass *falls für wenigstens einen Punkt* $x \subset C$ $ind_x\, C \geqq \aleph_0$ *ist, C unendlich viele geschlossene Jordankurven enthält* (da in diesem Falle wenigstens ein $K_j^* \subset \overline{D_1^*}$ mit $\overline{A_1^*}$ unendlich viele Punkte gemeinsam hat).

[2]) Falls dabei $ind_x\, C = \omega$ ist, so betrachten wir *jede* endliche Menge B als eine die erwähnten Minimaleigenschaft besitzende.

Menge $\tilde{B}$ von der, dem Werte $ind_x\, C$ entsprechenden Mächtigkeit. Wir betrachten nun die entsprechende ε-Aussonderung $C = \tilde{A} + \tilde{B} + \tilde{D}$. Wir haben erstens die Inklusionen $\overline{\tilde{A}} \subset A$, $\overline{\tilde{D}} \supset \overline{D}$; ferner ist jede Komponente K (von $\overline{D}$) in einer Komponente $\tilde{K}$ (von $\overline{\tilde{D}}$) enthalten. Wir bezeichnen jetzt diejenigen Komponenten $\tilde{K}$, die mindestens ein K enthalten, mit K^* und setzen Q_* gleich der Vereinigungsmenge sämtlicher K^*; wir bezeichnen weiter durch $K^{\odot}$ die von K^* verschiedenen Komponenten der Menge $\overline{\tilde{D}}$; ihre Vereinigungsmenge soll $Q_{\odot}$ heissen.

Dann ist:

$$\tilde{D} = Q_* + Q_{\odot} \quad ; \quad \tilde{B} = \tilde{B} \,.\, Q_* + \tilde{B} \,.\, Q_{\odot}.$$

Die Zerlegung

$$C = A_1 + B_1 + D_1$$

mit

$$A_1 = A + Q_{\odot},$$

$$B_1 = \tilde{B} \,.\, Q_*,$$

$$D_1 = Q_* - B_1,$$

ist eine ε-Aussonderung des Punktes x, was man in derselben Weise, wie beim Beweise des Satzes II, zeigt.

Diese ε-Aussonderung genügt aber den beiden Voraussetzungen in bezug auf die Komponentenzahl der Mengen $\overline{D_1}$ und B_1, w.z.b.w.

Es sei hierzu noch bemerkt, dass man stets verlangen kann, die Menge A_1 sei zusammenhängend: im entgegengesetzten Falle hätte man nur A_1 durch $\dot{A} = Komp_x\, A_1$ zu ersetzen [1]) und der Reihe nach $\dot{B} = \overline{\dot{A}} - \dot{A}$, $\dot{D} = C - (\dot{A} + \dot{B})$, und schliesslich

$$A_2 = \dot{A} + (B - \overline{\dot{D}})$$

$$B_2 = \dot{B} \,.\, \overline{\dot{A}} \,.\, \overline{\dot{D}}$$

$$D_2 = \dot{D} + (\dot{B} - \overline{\dot{A}})$$

zu definieren [2]). Man kann dies wie folgt zusammenfassen:

Satz IV. *Für jeden Punkt x einer stetigen Kurve C und für jedes $\varepsilon > 0$, gibt es ε-Aussonderungen, welche gleichzeitig Minimaleigenschaften in Bezug auf die Komponentenzahl der Mengen $\overline{A}$, B und $\overline{D}$ besitzen* [3]).

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[1]) Es ist zu bemerken, dass letztere Menge auf Grund eines bekannten Satzes von HAHN in bezug auf C offen ist.

[2]) Man beweist in der Tat leicht, dass erstens $B_2 \subset B_1$ ist, zweitens jede Komponente von D_2 mit B_2, also mit B_1 gemeinsame Punkte hat, und folglich eine Komponente von $\overline{D_1}$ enthält. Daraus folgen aber beide Minimaleigenschaften für $C = A_2 + B_2 + D_2$.

[3]) Nur 0-dimensionale Mengen B werden dabei zur Konkurrenz zugelassen (vgl. auch die Fussnote [1]), Seite 1252).

Diese ε-Aussonderungen werden wir als *„normal"* bezeichnen.

Wir sind jetzt im Stande, die beiden Indices zu vergleichen, und führen dazu die neue Zahl

$$\triangle_x C = ind_x\, C - Ind_x\, C$$

ein.

Wenn $ind_x\, C$ endlich ist, ist die Bedeutung von $\triangle_x C$ klar.

Falls $ind_x\, C = \omega$ ist, setzen wir $\triangle_x\, C$ definitionsgemäss gleich der kleinsten Zahl $\alpha \leqq \infty$ von der Beschaffenheit, dass es für jedes $\varepsilon > 0$ eine normale ε-Aussonderung $C = A + B + D$ gibt, für die $\beta - \delta \leqq \alpha$ ist (wobei β bzw. δ die Anzahl der Komponenten von B bzw. $\overline{D}$ bedeutet).

Falls endlich $ind_x\, C \geqq \aleph_0$ ausfällt, so ist das einzig-vernünftige $\triangle_x\, C$ (dem Satze II entsprechend) gleich $ind_x\, C$ zu setzen.

Satz V. *Wenn C und C^* zwei stetige Kurven sind und $C \supset C^* \supset x$, so ist $\triangle_x\, C \geqq \triangle_x\, C^*$.*

Beweis. Offenbar ist $ind_x\, C \geqq ind_x\, C^*$. Die Ungleichung $\triangle_x\, C \geqq \triangle_x\, C^*$ folgt alsdann für $ind_x\, C \geqq \aleph_0$ aus der Definition selbst. Bleibt übrig den Satz für den Fall $ind_x\, C \leqq \omega$ zu beweisen.

Es sei $C = A + B + D$ eine normale, dem Werte von $\triangle_x\, C$ entsprechende ε-Aussonderung des Punktes x. Die Zerlegung $C^* = A^{**} + B^{**} + D^{**}$, wobei $A^{**} = A \,.\, C^*$, $B^{**} = B \,.\, C^*$, $D^{**} = D \,.\, C^*$ gesetzt ist, ist dann wieder eine ε-Aussonderung von x in bezug auf C^*. Es ist ausserdem $A^{**} \subset A$, $B^{**} \subset B$; $D^{**} \subset D$.

Falls B^{**} Punkte ausserhalb $\overline{A^{**}} \,.\, \overline{D^{**}}$ enthält, so fügen wir diese Punkte zu D^{**} bzw. A^{**} hinzu. Die so erhaltenen Mengen bezeichnen wir wieder mit A^{**}, B^{**}, D^{**}. Es seien β, δ bzw. β^{**}, δ^{**} die diesen Aussonderungen entsprechenden Anzahlen von Komponenten (wobei nicht zu vergessen ist, dass die Menge B (also auch B^{**}) aus endlichvielen Punkten besteht).

Wir haben immer $\beta \geqq \beta^{**}$. Wenn dabei $\delta \leqq \delta^{**}$, so ist $\beta - \delta \geqq \beta^{**} - \delta^{**}$. Wir werden aber gleich sehen, dass letztere Ungleichung auch für den Fall $\delta > \delta^{**}$ gilt. Es seien in der Tat $K_1^{**}, K_2^{**}, \ldots K_{\delta^{**}}^{**}$ die Komponenten von $\overline{D^{**}}$, und $K_1, K_2, \ldots K_{\delta^{**}}$ die, durch die Inklusionen $K_i \supset K_i^{**}$ $(i = 1, 2, \ldots \delta^{**})$ eindeutig bestimmten Komponenten von $\overline{D}$. (Zwei mit verschiedenen Indizes versehene K_i können dabei selbstverständlich identisch sein). Unserer Voraussetzung gemäss gibt es jedenfalls $\delta - \delta^{**}$ von allen $K_1, \ldots K_{\delta^{**}}$ verschiedene Komponenten $K_{\delta^{**}+1}, \ldots K_\delta$ der Menge $\overline{D}$. Jede dieser Komponenten hat mit B wenigstens einen Punkt gemein. Daraus folgt, dass

$$\beta - \beta^{**} \geqq \delta - \delta^{**} > 0,$$

und also

$$\beta - \delta = [\beta^{**} + (\beta - \beta^{**})] - [\delta^{**} + (\delta - \delta^{**})] \geqq \beta^{**} - \delta^{**}$$

ist.

Die Aussonderung $C^* = A^{**} + B^{**} + D^{**}$ ist im allgemeinen keine normale. Man kann sie aber normalisieren, so wie es beim Beweise der Sätze III und IV gezeigt wurde. Es sei $C^* = A^* + B^* + D^*$ die so entstandene normale ε-Aussonderung und β^*, δ^* ihr entsprechende Anzahlen von Komponenten. Dabei nimmt, für genügend kleine ε, die Zahl $\beta^{**}-\delta^{**}$ während des ganzen Prozesses der Normalisierung niemals zu, [1]) so dass $\beta^{**}-\delta^{**} \geqslant \beta^* - \delta^*$ ist.

Also haben wir $\triangle_x C \geqslant \beta - \delta \geqslant \beta^{**}-\delta^{**} \geqslant \beta^* - \delta^*$, wobei $\beta^* - \delta^*$ einer normalen ε-Aussonderung auf C^* entspricht. Die Zahl $\triangle_x C$ genügt der für $\triangle_x C^*$ charakteristischen Ungleichung. Da $\triangle_x C^*$ die kleinste Zahl von dieser Beschaffenheit ist, so ist $\triangle_x C \geqslant \triangle_x C^*$, w.z.b.w.

Aus dem Satze V folgt

Satz VI. *Damit eine stetige Kurve C eine Baumkurve* [2]) *sei, ist notwendig und hinreichend, dass für sämtliche Punkte $x \subset C$ die Gleichung $\triangle_x C = 0$ gilt.*

Die Bedingung ist hinreichend. In der Tat, falls C eine einfache geschlossene Linie C^* enthält, so gilt für jeden Punkt $x \subset C^*$ die Gleichung

$$\triangle_x C^* = 1\,;$$

also ist nach dem Satze V $\triangle_x C \geqslant 1$.

Die Bedinging ist notwendig. Wir setzen voraus, dass C eine Baumkurve ist, für die in irgend einem Punkte $x \subset C$, $\triangle_x C \geqslant 1$ ausfällt.

Es sei nun $C = A + B + D$ eine normale ε-Aussonderung (wobei ε klein genug ist damit $\beta - \delta > 0$ sei). Mindestens eine Komponente K von $\overline{D}$ enthält zwei Punkte von B, z.B. b_1 und b_2. Da K ein im kleinen zusammenhängendes Kontinuum ist [1]), kann man b_1 mit b_2 durch einen in K enthaltenen einfachen Bogen S_1 verbinden. Da aber $A + B$ auch ein im kleinen zusammenhängendes Kontinuum ist, so kann man auch einen in $A + B$ enthaltenen, b_1 mit b_2 verbindenen einfachen Bogen S_2 finden. $Q = S_1 + S_2$ ergibt dann eine in C enthaltene einfache geschlossene Linie, was unsrer Voraussetzung widerspricht.

Wir wollen jetzt folgenden Satz beweisen:

Satz VII. *Damit eine stetige Kurve C eine und nur eine einfache geschlossene Linie Q enthält, ist notwendig und hinreichend, dass die beiden folgenden Bedingungen gleichzeitig erfüllt sind:*

1⁰. *Für jeden Punkt $x \subset C$ ist $\triangle_x C \leqslant 1$.*

2⁰. *Die Menge M aller Punkte $x \subset C$, in denen $\triangle_x C > 0$ ist, ist zusammenhängend.*

Bevor wir die Notwendigkeit unserer beiden Bedingungen beweisen, bemerken wir, dass falls C *nur* eine einfache geschlossene Linie enthält, sicher für alle Punkte $x \subset C$ die Ungleichung $ind_x C \leqslant \omega$ gilt [3]). *Beim*

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[1]) Für den Fall $ind_x C^* = \omega$ besteht der erwähnte Prozess aus einem einzigen Schritte, man setzt nämlich $A^* = Komp_x A^{**}$ (vgl. auch Fussnote [1]) auf Seite 1255).

[2]) Man versteht unter einer *Baumkurve* eine, keine einfache geschlossene Linie (= geschlossene JORDANkurve) enthaltende stetige Kurve. Diese Kurvenart wurde zuerst von MAZURKIEWICZ und sodann von MENGER (l.c.), von dem auch die Bezeichnung "Baumkurve" herrührt, untersucht. (Vgl. Fund. Math. 2, S. 119).

[3]) Siehe Fussnote [1]) auf S. 1255.

Beweise der Notwendigkeit unsrer Bedingungen dürfen wir also annehmen, dass C eine endlich verzweigte[1] *Kurve ist.*

Die Bedingung 1^0 ist notwendig. Es sei in der Tat C eine endlich verzweigte stetige Kurve, die eine einzige einfache geschlossene Kurve Q enhält und die in wenigstens einem Punkte x der Bedingung $\triangle_x C \geqq 2$ genügt. Wir wollen zeigen, dass dies unmöglich ist.

Zwei Fälle sind a priori möglich.

1^0. Der Punkt x ist nicht in Q enthalten.

2^0. Der Punkt x gehört zu Q.

Wir untersuchen zuerst den Fall 1^0. Es sei $U(x)$ eine der Bedingung $\overline{U}(x) \,.\, Q = 0$ genügende *zusammenhängende* Umgebung des Punktes x (rel. C). Dann ist $C_0 = \overline{U}(x)$ eine Baumkurve und es gibt (infolge des Satzes VI) eine normale ε-Aussonderung ($\varepsilon < \varrho\,(x, C - U\,(x))$ des Punktes x (in Bezug auf C_0)

$$C_0 = A_0 + B_0 + D_0,$$

wobei die Komponentenzahl δ_0 von $\overline{D}_0$ gleich der (endlichen) Anzahl β_0 von Punkten der Menge B_0 ist. Wir setzen nun $A = A_0$, $B = B_0$, $D = C - (A + B)$ und überzeugen uns ohne Schwierigkeit davon, dass

$$C = A + B + D$$

eine ε-Aussonderung der Punktes x in bezug auf C ist.

Ich behaupte nun, dass die Komponentenzahl δ von $\overline{D}$ gleich δ_0 ist. In der Tat, da jede Komponente von $\overline{D}$ mit $B = B_0$, also mit $\overline{D_0}$ gemeinsame Punkte hat, so ist sicher $\delta \leqq \delta_0$. Falls aber $\delta < \delta_0$ wäre, so würden gewiss zwei Komponenten K_1 und K_2 von $\overline{D_0}$ zu einer Komponente K von $\overline{D}$ gehören; da aber (wegen $\beta_0 = \delta_0$) K_1 und K_2 in verschiedenen Punkten b_1 und b_2 von B münden, so hat K mit B wenigstens diese beiden Punkte gemein. Indem wir nun b_1 und b_2 zuerst in K und dann in C_0 mittels zweier einfacher Bogen verbinden[2], erhalten wir sofort eine einfache geschlossene Linie Q_1, die mit C_0 gemeinsame Punkte hat und also sicher von Q verschieden ist. Im Falle 1^0 würde also C im Widerspruch zu unsrer Voraussetzung mindestens zwei verschiedene einfache geschlossene Linien Q und Q_1 enthalten.

Wir wenden uns jetzt zum Falle 2^0: $x \subset Q$ und betrachten eine bestimmte ε-Aussonderung $C = A + B + D$ des Punktes x, wobei

$$B = \sum_1^{\beta} b_i\,, \qquad \overline{D} = \sum_1^{\delta} K_i\,, \qquad \beta - \delta \geqq 2$$

ist.

Ohne die Allgemeinheit einzuschränken dürfen wir in unsrem Falle annehmen, dass die Menge $B \cdot Q$ nur aus zwei Punkten, z.B. aus b_1 und b_2 besteht. Dann folgt aus $\beta - \delta \geqslant 2$ leicht, dass

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[1] Eine Kurve C heiszt *endlich-verzweigt* (URYSOHN) falls für jeden ihrer Punkte $\text{ind}_x\, C \leqq \omega$ ist. Bei MENGER (l.c.) wird eine derartige Kurve „regulär" genannt.

[2] Dies ist stets möglich, da jedes Teilkontinuum einer endlich verzweigten Kurve selbst endlich verzweigt, also im kleinen zusammenhängend ist (Siehe URYSOHN, II, ch. III; MENGER, Math. Ann. 95, S. 300.

I. entweder die Komponente von $Q - A$ in $\overline{D}$, d.h. die grösste zusammenhängende, $Q - A$ enthaltende Teilmenge K von $\overline{D}$, mindestens einen, von beiden Punkten b_1 und b_2 verschiedenen Punkt $b_i \subset B$ enthält

II. oder eine von K verschiedene Komponente K^* der Menge $\overline{D}$ zwei (von den Punkten b_1, b_2 nicht notwendig verschiedene) Punkte $b_p + b_q \subset B$ enthält.

In beiden Fällen gibt es, wie leicht beweisbar, eine von Q verschiedene einfache geschlossene Linie $Q^* \subset C$, was der Annahme widerspricht.

Die Bedingung 2^0 ist notwendig. In der Tat, falls C nur eine geschlossene JORDANkurve Q enthält, so folgt aus VI leicht, dass für $x \subset C - Q$ stets $\triangle_x C = 0$ ist. Da andererseits für jeden Punkt $x \subset Q$ $\triangle_x C \geqslant \triangle_x Q = 1$ ist, so ist M mit Q identisch, also zusammenhängend.

Die Bedingungen 1^0 und 2^0 sind hinreichend. Aus 1^0 folgt wieder $ind_x C \leqslant \omega$. Nehmen wir an, C enthalte zwei oder mehrere einfache geschlossene Linien, $C \supset Q_1 + Q_2 + \ldots$ Wir beweisen zuerst, dass wenigstens zwei dieser Linien gemeinsame Punkte haben. Im Falle, wo C nur endlichviele einfache geschlossene Kurven enthält, folgt letztere Behauptung unmittelbar aus unsren Voraussetzungen (weil dann, wie leicht ersichtlich, M mit der Vereinigungsmenge aller in C enthaltenen geschlossenen Kurven identisch ist).

Es seien nun in C unendlich (und dann notwendig nur abzählbar) viele geschlossene JORDANkurven

$$Q_1, Q_2, \ldots, Q_n, \ldots$$

enthalten, die paarweise zueinander fremd sind. Offenbar ist (auf Grund von Satz V) $\Sigma Q_n \subset M$. Ich behaupte, dass auch umgekehrt $M \subset \Sigma Q_n$ ist, m. a. W., dass für jeden Punkt $x \subset C - \Sigma Q_n$

$$\triangle_x C = 0$$

ist. Es sei in der Tat C^* diejenige *Baumkurve*, die aus C dadurch entsteht, dass man jede Kurve Q_n durch einen einzigen Punkt x_n^* ersetzt und alle sonstigen Limesbeziehungen in C unverändert in C^* aufnimmt (so dass C^* ein eindeutiges stetiges Bild von C, und $C^* - \sum\limits_{n=1}^{\infty} x_n^*$ ein eineindeutiges Bild von $C - \Sigma Q_n$ ist).

Dann ist für jeden Punkt $x \subset C - \sum\limits_{n=1}^{\infty} Q_n$

$$\triangle_x C = \triangle_{x^*} C^* = 0 \quad (x^* \text{ ist der Bildpunkt von } x \text{ in } C^*),$$

womit unsre Behauptung bewiesen ist.

Es können also in C unmöglich lauter zueinander fremde geschlossene JORDANkurven enthalten sein, so dass es in C mindestens zwei gemeinsame Punkte besitzende einfache geschlossene Linien Q_1 und Q_2 gibt.

Die Summe $Q_1 + Q_2$ bildet ein Kontinuum (stetige Kurve) $C_0 \subset C$. Nach dem Satze V bleibt nur noch übrig folgenden Hilfssatz zu beweisen:

Hilfssatz. *Wenn der Durchschnitt* $Q_1 . Q_2$ *von zwei verschiedenen einfachen geschlossenen Linien nicht leer ist, gibt es in* $Q_1 + Q_2 = C_0$ *Punkte, für die* $\Delta_x C_0 \geqslant 2$ *ist.*

Beweis. Da Q_1 und Q_2 verschieden sind, gibt es z.B. auf Q_1 einen offenen Bogen, der von Punkten von Q_2 frei ist. Wir bezeichnen jetzt mit S einen grössten diese Eigenschaft besitzenden Bogen. Dann ist für die Endpunkte a_1 und a_2 (die auch zusammenfallen können): $\Delta_{a_1} C_0 \geqslant 2$, $\Delta_{a_2} C_0 \geqslant 2$. Es genügt offenbar die Ungleichung $\Delta_{a_1} C_0 \geqslant 2$ zu beweisen. Ist a_1 ein isolierter Punkt von $Q_1 . Q_2$, so können wir ihn für genügend kleine ε durch vier (und nicht weniger) Punkte (zwei auf Q_1 und zwei auf Q_2) aussondern. Die zu A komplementäre Menge $\overline{D}$ enthält aber höchstens zwei Komponenten $Q_1 - A$ und $Q_2 - A$.

Ist dagegen a_1 kein isolierter Punkt von $Q_1 . Q_2$, so braucht man um ihn für ein hinreichend kleines ε auszusondern drei Punkte (zwei auf Q_2, von denen einer auf $Q_1 . Q_2$ zu wählen ist, und einen auf $S \subset Q_1$). Die zu A komplementäre Menge D kann aber dabei stets zusammenhängend vorausgesetzt werden. In beiden Fällen haben wir $\Delta_{a_1} C^* \geqslant 2$. Der Hilfssatz und der Satz VIII sind damit vollständig bewiesen.

Ist C eine ebene stetige Kurve, so gibt uns die Anwendung des Jordanschen Kurvensatzes die den Sätzen VI und VII analogen Sätze VI′ und VII′:

Satz VI′. *Damit eine ebene stetige Kurve* C *die Ebene nicht zerlegt, ist notwendig und hinreichend, dass für sämtliche Punkte* $x \subset C$ $\Delta_x C = O$ *ist.*

Satz VII′. *Damit eine ebene stetige Kurve* C *die Ebene in zwei Gebiete zerlegt ist notwendig und hinreichend, dass die beiden folgenden Bedingungen gleichzeitig erfüllt seien:*

1°. *Für jeden Punkt* $x \subset C$ *ist* $\Delta_x C \geqslant 1$.

2°. *Die Menge* $M = \{x, \Delta_x C > 0\}$ *ist zusammenhängend.*

Diese beiden Sätze können auch direkt (aber ziemlich umständlich) durch systematische Anwendung der Sätze von JANISZEWSKI und STRASZEWICZ bewiesen werden.

Moskau, 15. V. 1926.

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Biochemistry. — *"On the spreading of fatty acids, fats and proteins."*
By Prof. E. GORTER and F. GRENDEL. (Communicated by Prof. P. EHRENFEST.)

(Communicated at the meeting of October 30, 1926).

I.

The spreading of fatty acids.

The results of our experiments on the spreading of different substances on a watersurface, are not completely comparable to those obtained by other workers, because we have examined substances which are insoluble in ether, petroleumether or other like substances.

The greater part of the experimenters have dissolved the substances of which they studied the spreading on a watersurface in a solvent, that spreads itself and evaporates very quickly from the watersurface. We however have examined the area of the spreading of substances dissolved in water; all be it that these solutions were mostly colloidal ones.

In order to enable us to put our results on a firm basis, we have made a first series of experiments with substances which are soluble in petroleumether and of which also colloidal watery solutions can be prepared.

We have chosen for this purpose different fatty acids and have studied separately:

1°. the influence of the acidity of water on which the spreading takes place;

2°. the influence of the temperature of water on which the spreading was performed.

As fatty acids we have chosen palmitic acid, oleic acid and lauric acid and we have compared the spreading of these substance of their solutions in petroleumether with the spreading of the watery soap solutions which have been prepared by dissolving the corresponding fatty acid in the minimum amount of caustic soda solution. Both solutions were of the same strength $^1/_{100}$ mol.

As a result of these experiments one important fact is to be noted, that it is possible to obtain a spreading which is considered by everybody as a monomolecular one, by making use of a colloidal soapsolution. It is however necessary to observe certain precautions. One of the technical precautions that are of great importance is that only a very small quantity measured in a capillary pipette (we made use of a pipette of 0.005 c.c. divided in 10 parts) must be used, and this pipette must be held at the surface of the water in the tray and blown out in a horizontal position. A second condition which is necessary to observe is that the water in the tray is strongly acid. This acid not only serves to set free the fatty acid, but also to promote the spreading so as to make it maximal. The third condition is that the suitable temperature is chosen, which is different for different acids. Fatty acids with a short chain must be examined at a lower temperature than fatty acids with a longer chain. For these latter substances it is necessary to take account of the fact, described by ADAM that fatty acids exist in two forms: condensed and expanded.

From the correspondence between the numbers for the maximal spreading, obtained in the two series of experiments it is allowed to conclude that also the results with colloidal watery solutions are reliable.

Let us examine first of all the influence of the acidity of the water at 15° on the *spreading* of a certain fatty acid like *palmitic acid*, and observe if there is a difference between the spreading of a measured quantity of the petroleumether solution and the colloidal watery palmitic-soap solution.

On fairly acid solutions of a PH 2 ($^1/_{100}$ n. HCl acid) the spreading is maximal: the area per molecule is 20 sq. A. U. If we take solutions of hydrochloric acid that are of a lower acidity we find that in both cases the area is smaller. Whereas with petroleumether solutions these differences are of minor importance, the area occupied, when spreading from a watery soap-solution, are much smaller, so that a palmitic soap spread on distilled water occupies a surface that is only a small part ($^1/_3$ or $\frac{1}{4}$) from the maximal monomolecular-area. Moreover the results are not far as constant as when the maximal spreading is studied. This imperfect spreading that can be obtained under different conditions seems to be due to the existence of colloidal aggregates of molecules which orientate their polar groups to an outer surface.

Now the explanation of these too small numbers is a very dangerous question, for there are several other reasons for finding a too small area. We mention the solubility of the soap in the water of the tray and insufficient spreading due to insolubility, so that the polar group is so to speak insoluble. We have met with both reasons for imperfect spreading in our experiments. It is possible to recognize the first reason of smaller numbers than the mono-molecular layer would have given, by studying the influence of time and of compression. If the substance is too soluble to give a beautiful spreading the area tends to diminish in size by waiting. Besides compression of the films by laying more weights in the pan of the balance produces a considerable decrease of the area occupied, and this change is not wholly reversible. Often the pressure-area curve is not straight as with well-spreading substance but convex to the axis, so that it has more or less the form of a $p \cdot A = k$-line. We leave out of consideration whether this solution is a molecular or colloidal one, although the latter form of solution seems to have the highest probability.

The second reason why smaller numbers are found than a mono-molecular film would have given, can sometimes be recognized by a careful inspection of the surface and by seeing some small solid particles floating on the surface. In this case compression has the effect to break the film at a lower force than usually, whereas the pressure-area-curve tends to become concave towards the axis, thus presenting the reverse form from the foregoing case.

Soap solutions or fatty acids set free from these soap-solutions form surface films presenting a rather high compressibility, and often show an increase in size as a function of time, and are influenced by the same factors such as acidity temperature and pressure as ordinary mono-molecular films do. But not always the effect of these factors is the same in both cases.

It seems possible to describe all observed phenomena using a scheme of the following form.

There exists a gradual transition between substances of a certain series, say the fatty acids of the saturated series $(C_n H_{2n} O_2)$ also with regard to their spreading. Whereas the lower members are soluble the next ones form colloidal solutions, then we meet with fatty acids showing what we should like to call a colloidal spreading, followed by the group of well-spreading members, and ultimately we meet with substances, showing an imperfect spreading. We can thus give this series :

1	2	3	4	5
molecular solution	colloidal solution	colloidal spreading	mono-molecular spreading	imperfect spreading.

A fatty acid having a high number of C-atoms in the chain is placed to the right side whereas a lower member is placed more to the left hand side. If several chains are linked together, a displacement to the right, results. (If the polarity of a substance is lessened e.g. through esterification, the effect is a displacement to the right.) If now we study the influence of temperature we find that a lowering of temperature has the effect of a displacement to the right side of the above series. So a substance which shows a colloidal spreading at say 15°, can present a normal mono-molecular spreading at zero, and another fatty acid or fat, which shows a colloidal spreading at 15°, is dissolved in a colloidal form by heating. Also the influence of a change in the hydrogenion concentration of the water may be described in the same simple form, and we are justified to say that an increase of the acidity has the effect of a displacement to the right side of the series. A fatty acid or soap showing a colloidal spreading at a PH 4 will spread beautifully when blown out on water of PH 1. In other terms acidity promotes the spreading of a fatty acid.

How are all these influences to be explained? The tendency to spread is the consequence of two antagonistical factors: the solubility of the polar group in the water acts in orders to dissolve the molecule in the water, but its influence is counter-balanced by the action of the bounds between the C-atoms in the chain, that tends to keep the molecule out of the water.

This view makes it comprehensible that a substance with a lower number of C-atoms is more easily soluble than a substance with a higher number of C.-atoms. It explains that a fall of temperature has the same effect as an increase of the length of the chain, because the solubility diminishes through a fall of temperature. It makes plausible that an increase of the acidity of the water promotes the spreading because the polar groups are attracted with a smaller force, diminishing the solubility of these groups.

In all the foregoing résumé no mention had been made of the change of a substance from the condensed to the expanded condition. If we study this phenomenon, we first of all must mention the remarkable fact already observed by ADAM, that the point of half-expansion is not the same as the melting point, but is in all members of the series much lower. We have come to the conclusion that nevertheless this transition between expanded and condensed condition is so to speak a bi-dimensional melting. We must try to explain why this bi-dimensional melting takes place at a lower temperature than the tri-dimensional. It seems that this difference is principally due to the fixation of the polar groups of the fatty acids to the water. This fixation at the water has the effect of diminishing the strength, with which the molecules are kept together and so it must be admitted that the COOH-groups contribute to this latter property. This seems not improbable, if we compare the melting points of a series of fatty acids to the same series of methylated fatty acids or to the paraffine-series. Always the melting points are highest in the series of substances having the COOH-groups in the molecule.

This hypothesis is strengthened by the very remarkable observation, that the acidity of the water in the tray has a very distinct influence on this bidimensional melting point: On acid water ($^1/_{10}$ n. HCl.) the melting point is much lower than on distilled water. The acid produces this effect by loosening the bounds between the molecules, as it has a greater influence on the polar groups than water has.

We give the figures for palmitic and acid (fig. 1, 2 and 3).

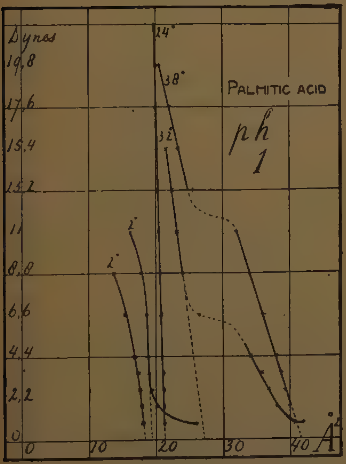


Fig. 1

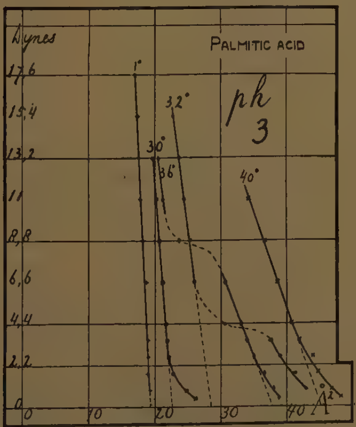


Fig. 2.

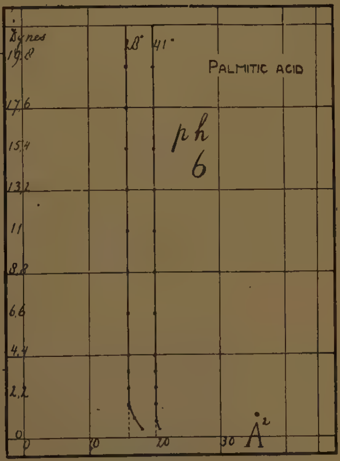


Fig. 3.

In concordance with this hypothesis is the fact that the compressibility of the "expanded" substance, spread on water, is much higher than that of the same substance in its condensed condition. Besides it is striking that lower members of the series of fatty acids, whose spreading is promoted by lowering the temperature or by using strongly acid water, always show a behavior of expanded substances and thus occupy a larger area and present a greater compressibility (fig. 4, 5 and 6).

We give as an example the spreading of lauric acid on strongly acid water.

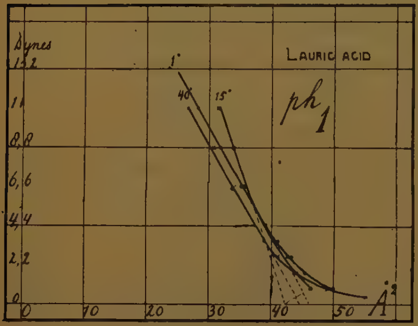


Fig. 4.

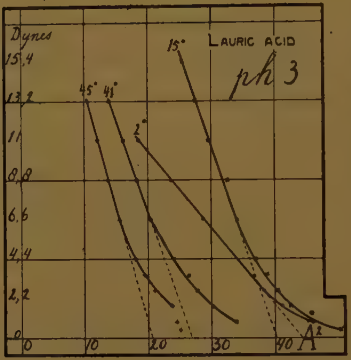


Fig. 5.

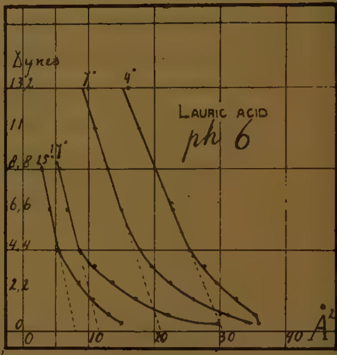


Fig. 6.

The following figures show how the mono-molecular spreading of soaps can only be obtained on strongly acid water (fig. 7—12).

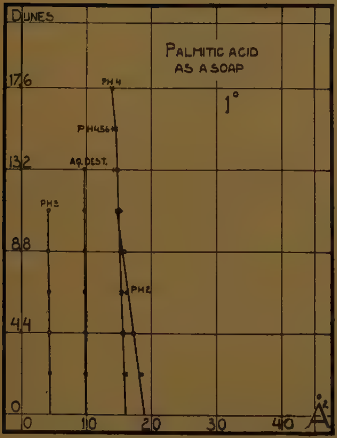


Fig. 7.

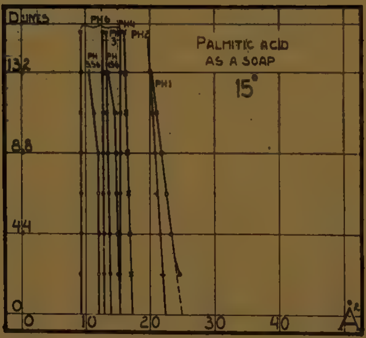


Fig. 8.

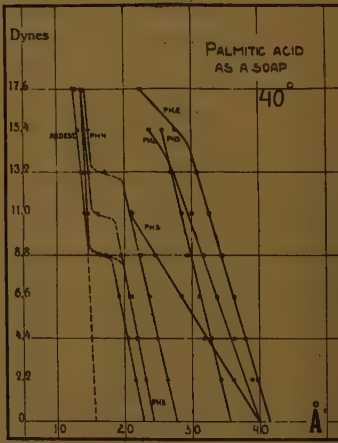


Fig. 9.

A very clear impression is given by plotting the PH of the water in the tray against the area occupied by the soaps (fig. 13 and 14).

We now come to the very important question as to the meaning of the small numbers encountered for the soap-spreading. We are inclined to ascribe these small areas to an association of the soap-molecules in some form that persists on the surface of the water in the tray. By using strongly acid water, this association is broken, and on ordinary distilled water or on a hydrochloric acid solution of a PH 3, the molecules remain associated.

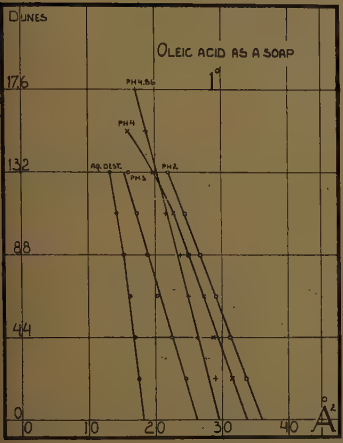


Fig. 10.

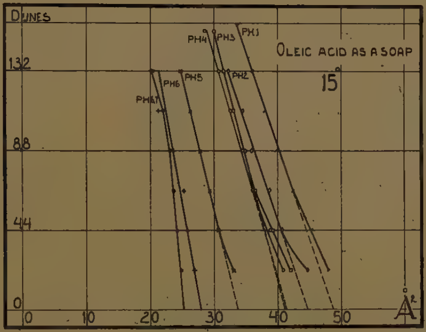


Fig. 11.

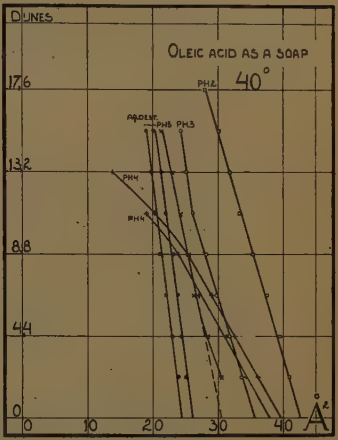


Fig. 12.

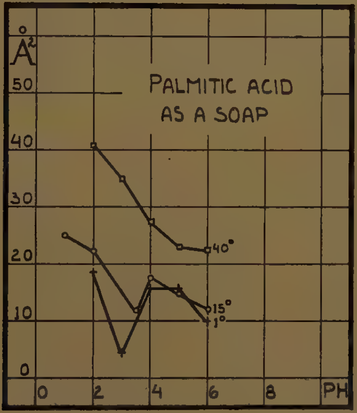
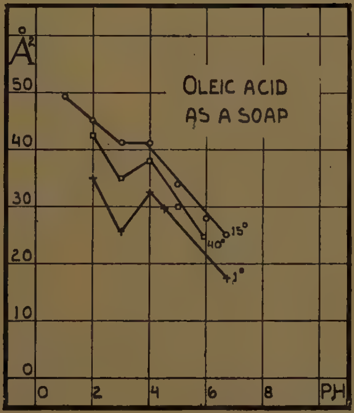


Fig. 13.



Fiq. 14.

In this line of thought it is possible to admit that the associated molecules turn the polar groups towards an outer surface and that the spreading of these aggregates is due to these superficially placed groups. In good agreement with this view is the fact that the smaller spreading often is $^1/_3$ of the mono-molecular one. This number is to be expected if the soap-molecules are placed with the carbon chains in touch of each other and the (broader) COONa-groups in the outside: so forming globes, whose outer surface is entirely constituted of COONa polar groups, thus rendering the particle soluble.

Another fact deserves mention in this respect that fatty acids dissolved in alcohol and spread out on distilled water, often give values, that are far too small and again show a real mono-molecular spreading if blown out on strongly acid water. This is what might be expected from the boiling point determinations of such kind of substances, which are abnormal and are generally explained by admitting an association of molecules.

II.

On the spreading of fats.

Before describing the experiments with proteins, we wish to add a few words on the spreading of fats.

If we examine different representatives of the triglycerides of the saturated series, we find the same influence of the length of the chain and of the temperature on the area occupied at a water-surface whereas, however, the influence of a change in acidity of the water is of far less importance owing to the COOH groups being replaced by CO—OC groups.

In comparing the length of the chain, where the mono-molecular spreading begins, we find that already 6 C-atoms suffice to render the

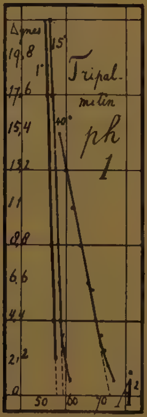


Fig. 15.

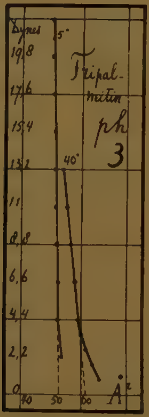


Fig. 16.

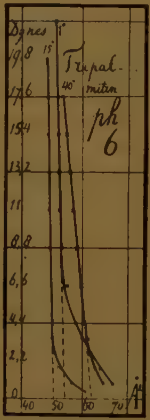


Fig. 17.

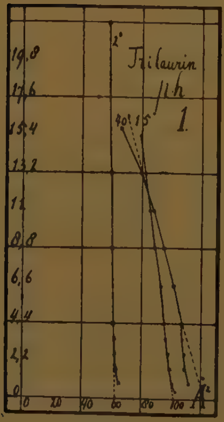


Fig. 18.

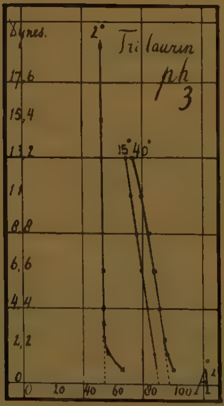


Fig. 19.

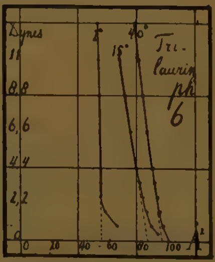


Fig. 20.

molecule sufficiently stable to enable a perfect spreading. This leads to the conclusion that the tendency to spreading is highly ameliorated by the linkage of three chains. We also detect the same difference in area and compressibility between the lower and the higher members of the series.

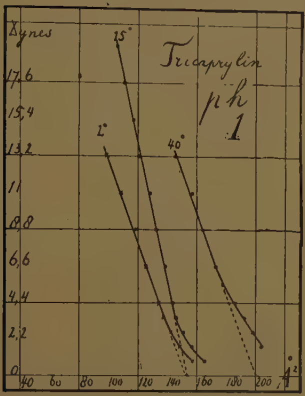


Fig. 21.

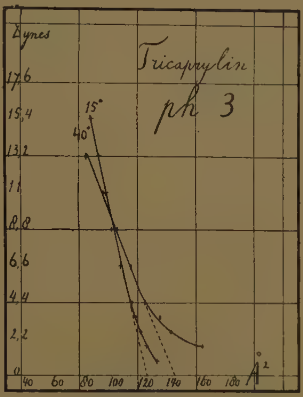


Fig. 22.

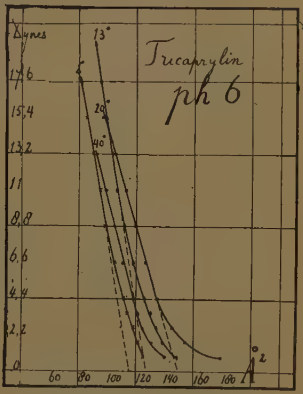


Fig. 23.

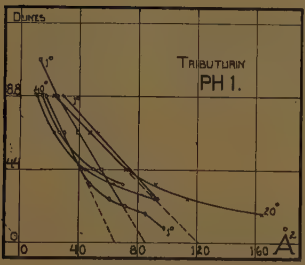


Fig. 24.

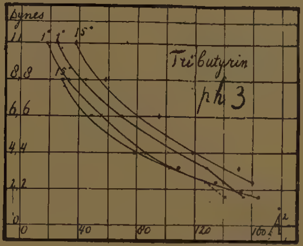


Fig. 25.

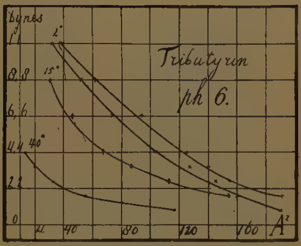


Fig. 26.

Tripalmitin[1] (C 16) spreads in a condensed form even at a temperature of 40°, trilaurin (C 12) has a condensed form only at 1°, but is in an intermediary condition at 15°. Tricaprylin (C 8) already at 15° C. occupies an area of 120 sq. A.U., (60 sq. A.U. being the value for the spreading of a fat in a condensed state). Finally tributyrin only spreads at a low temperature, 1°, whereas at a higher temperature it spreads colloidally or not at all. (Fig. 15—26.) Neither on the transition of the condensed to the expanded state, nor on the spreading itself, has the acidity of the water any important influence. Where it exists the influence is of the same order as with fatty acids: acidification of the water in the tray promotes the expansion and increases the area occupied on the watersurface.

III.

On the spreading of proteins.

The observations on the spreading of proteins are based on the results obtained in studying soaps and fatty acids. It has been shown that it is possible to obtain a mono-molecular spreading even when using colloidal solutions, if only care is taken to use strongly acid water and to choose a suitable temperature.

The results were proven to be highly dependent on the length of the fatty acid chain: at a length of 14 or 16 C-atoms mono-molecular spreading easily occurs at any temperature. This temperature only exerts its influence on the mode of spreading, namely whether in a condensed or in an expanded form. With the lower members of the series (C 12) mono-molecular spreading is only seen at a higher acidity or at a lower temperature. Now in comparing fatty acids with fats having the same number of C-atoms, we found that spreading is far more easily arrived at as with fats, as already short-chained members give a perfect spreading. Moreover with the lower fatty acids (under C 10) and fats (under C 6) the numbers indicating the area occupied are too small and by increasing the temperature the area diminishes still more. This fact already indicates a solution.

Now we still believe that at a certain temperature and for a certain length of the chain it is possible to admit a colloidal mode of spreading, an expression used by us to indicate that associated molecules having their polar groups orientated to an outer surface can prefer to stay at the surface instead of disappearing in the water of the tray under the surface. They can remain at the surface even when conglomerated in globes in which case values for the area occupied must be found of about $^1/_3$ that of the mono-molecular spreading, as has actually been found.

Let us now study the results of the protein-spreading in the light of the foregoing experiments. It appears first of all, that most proteins can be spread on a hydrochloric acid solution of a PH 1 (or 2) in a layer whose thickness is 7 to 8 A.U. In this calculation the assumed value for the molecular weight drops out. We admit that this maximal spreading is a real mono-molecular one. One often succeeds in obtaining this maximal spreading on water of a lower acidity, if the temperature of the water in the tray is higher.

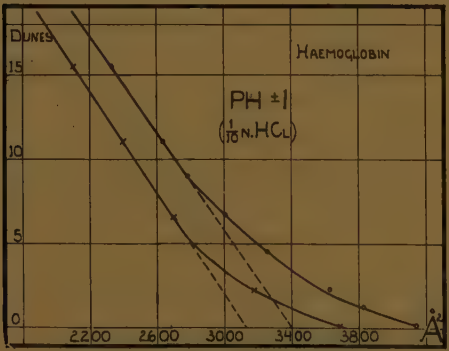


Fig. 27.
Haemoglobin (Mol. w. 16000)
Thickness at 3000 sq.A.U. 7 A. U.

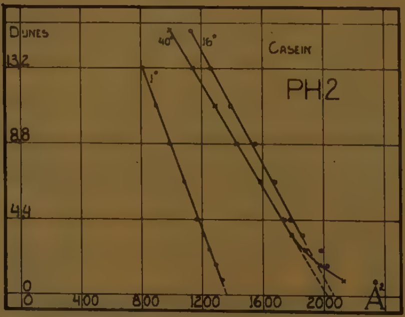


Fig. 28.
Casein (Mol. w. 12600)
Thickness at 2000 sq. A.U. 8 A.U.

We give some examples of this mono-molecular spreading. (Fig. 27, 28 and 29.)

Now it is impossible to obtain this maximal spreading in such thin films with every protein. We tend to admit that in analogy to what has been observed while studying fats, this different behavior of some proteins is due to a too small number of connected amino-acids or to a too great prevalence of short-chained amino-acids in the molecule. We give as examples *gelatin* and *gliadin*. (Fig. 30 and 31.)

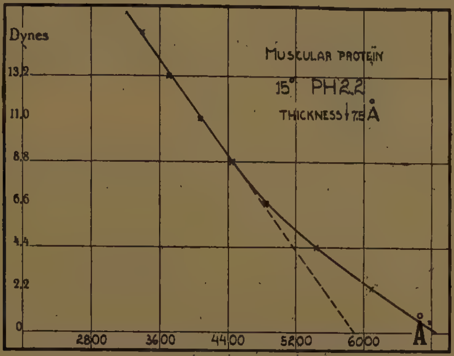


Fig. 29.
Serumprotein (Mol. w. 34000)
Thickness at 5800 sq. A.U. 7.6 A.U.

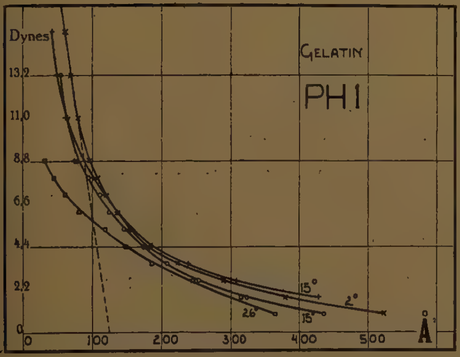


Fig. 30.
Gelatin (Mol. w. 10800)
Thickness at 450 sq.A.U.; 30 A.U.

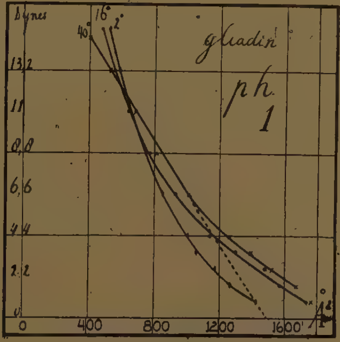


Fig. 31.
Gliadin (Mol. w. 12600)
Thickness at 1500 sq.A.U.: 10.5 A.U.

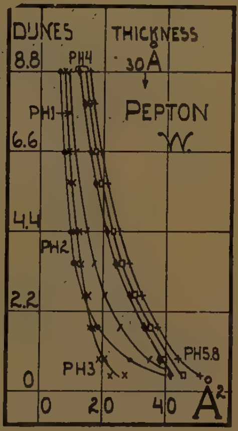


Fig. 32.
Peptone (Mol. w. 860)

Also *peptone* shows this same imperfect spreading. (Fig. 32.)

It is apparent that the spreading of gelatin is comparable to the spreading of tributyrin. They resemble us not only in so far that the size of the spreading is much too small, but also with regard to the form of the pressure-area curve, which is identical with both substances whereas heating has the same paradoxal influence to diminish the area by promoting the solution. In good agreement with this explanation is the fact that gelatin has a considerable quantity (25%) of glycocoll, thus possessing too many short-chained (2 C-atoms) amino-acids in its molecule.

Perhaps the circumstance that it is necessary to heat the gelatin-solution before putting it in the surface, has an influence on the final result. In peptone we meet with an example of a substance where the imperfect spreading is the consequence of both factors: a too small number of connected amino-acids must have the greatest importance here. Gliadin seems in a certain sense an intermediary form.

Before leaving the subject of the mono-molecular spreading we wish to emphasize that this spreading is the consequence of the attraction towards the water of all polar groups principally the CO-NH groups. If we calculate what is the area on the avarage occupied by each amino-acid we obtain a value of 18 sq. A.U. in the case of such proteins as hemoglobin, or casein, which is exactly the expected value if all the CO-NH groups are orientated towards the water. Each carbon chain in a fat occupies an area of about the same value ± 21 sq. A.U.

We must add a few words on the remarkable fact, that according to the classical view the protein molecules are very large. For hemoglobin 16000 is too small a value, and from Adair's experiments 64000 seems the most probable value, so that each molecule would contain 4 Fe-atoms. For casein 34000 is the generally admitted value, but even here some experimental work seems to indicate, that a higher value is more probable. But even when we take the smallest number one is forced to consider the protein molecules — probably very plastic — as flat platelets or needles, when spread out on a water surface, whose thickness depends on the average length of the constituting amino-acids.

If now we examine the spreading of proteins at a different acidity or a lower temperature we encounter in the beginning considerable irregularity as to the results. Generally speaking we may say, that by diminishing the acidity of the water or by lowering temperature the area tends to diminish and hence the calculated thickness of the film is increased. Before getting any reproducible results it is however indispensable to take into

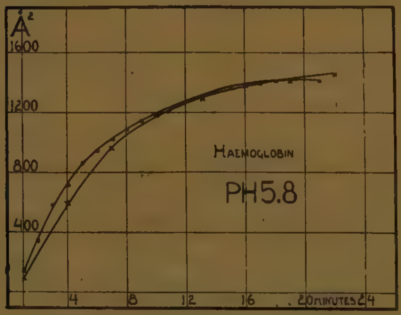


Fig. 33.

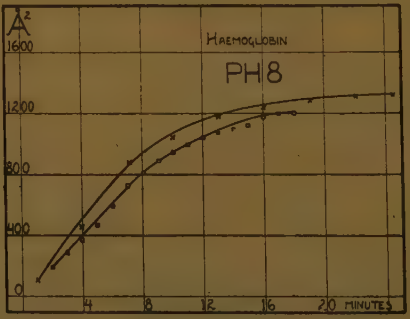


Fig. 34.

account the sometimes considerable influence of the time on the size of the area occupied.

This influence appeared most clearly in studying hemoglobin. (Fig. 33 and 34.)

But also in measurements of casein it is always necessary to reckon with the possibility of a slow reaching of the end-point of the spreading although it takes seldom more than 10 minutes, before the final definite spreading is obtained.

As a rule the mono-molecular maximal spreading either due to a higher temperature or to a higher acidity of the water in the tray, is almost immediate. This influence of time already indicates an association of molecules in the original solution.

We have very carefully studied the influence of acidity and temperature on the spreading of very pure casein (prepared in the laboratory of Prof. KRUIJT). We give the following figures expressing the very remarkable influence of change in acidity on the spreading of casein at different temperatures.

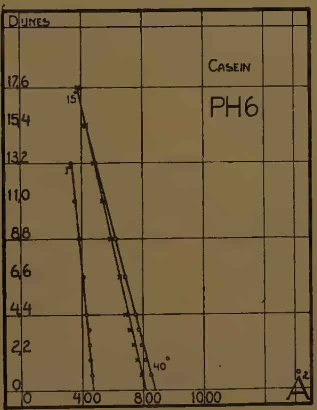


Fig. 35.

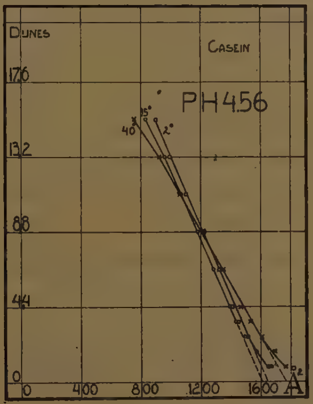


Fig. 36.

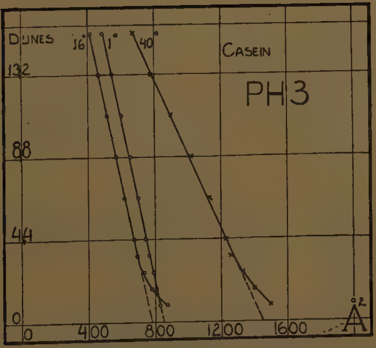


Fig. 37.

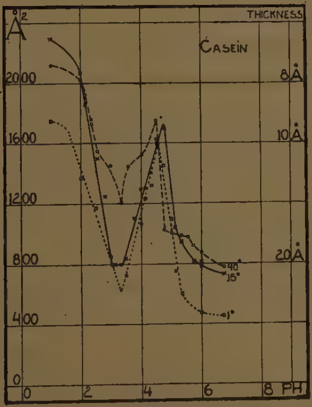


Fig. 38.

To give an idea of the compressibility of the protein films and the slope of the pressure-area curves under influence of temperature and acidity we give these experiments. The compressibility is of the same order of magnitude as of the „expanded" films of fatty acids (18—24 dynes). This fact does not imply, that proteins are considered as „expanded", because it is difficult to decide this point.

With regard to the figure indicating the influence of PH variations on the size of the protein-molecule, we wish to remark, that both casein and hemoglobin show two minima on both sides of the iso-electric point. Both proteins were dissolved with caustic soda and are therefore exactly comparable to the soap-solutions described above. We will show that the same explanations hold good. In the casein-sol several molecules are associated but in such a manner that they turn their polar groups to the outside. If we bring a very small amount of this casein-sol on freshly boiled distilled water this association remains unaltered. But if we spread the same casein-sol on more acid water, the casein is gradually set free, till at the iso-electric point the casein spreads in a mono-molecular layer. By further adding acid to the water, we obtain a change into strongly associated casein hydrochloride-molecules, who spread only in a monomolecular layer by considerable increasing the acidity of the water.

In certain experiments almost fortunately, with hemoglobine or with casein, muscle protein or serum protein we find a much smaller area per molecule, probable due to a higher degree of association. Only at a definite PH of the water and at a low temperature this small spreading is somewhat stabile. In most of the experiments in the beginning this small area is seen, but increases gradually when time is allowed to interfere. In those cases one is reminded the experiment of *Cary and Rideal*, who found the same mode of very slow spreading by making use of a crystal of stearic acid. We believe that this minimal spreading, where each molecule occupies an area of 100 sq. A.U. must be ascribed in the case of hemoglobin to an orientation of the molecules in such a manner that the prosthetic group is turned to the surface, and that the CO-NH groups of the different molecules lay side on side perhaps separated by a layer of water molecules. For the spreading of haematin itself gives a value of about 72 sq. A.U.

To increase the analogy between fats and proteins we add a few results obtained with lower members of the series of saturated fats. By X ray experiments we know that the transverse dimension of a fatty acid chain must be 4 A.U. Now some values obtained with tricaproin and tricaprylin are exactly those which would be expected by admitting a horizontal position of these fats on the water.

Palæontology. *"Figures of the Femur of Pithecanthropus Erectus".* (Plates I to IV). By Prof. EUG. DUBOIS.

(Communicated at the meeting of June 26, 1926).

The photographic figures 1 tot 6 and the röntgenograms, figures 8 and 9, of the femur of Pithecanthropus erectus, with the photographic figure 7 of a human femur for comparison, (Pl. I to IV) herewith published, serve to illustrate "the Principal Characters of the Femur of Pithecanthropus Erectus". (Proceedings Vol. **29**, p. 630—743), and conclude the illustration of all the fossil remains of Pithecanthropus hitherto discovered.

In the same way as the before published figures of the calvarium etc. [1]) these photos natural size were taken with the aid of the stereorthoscope (Proceedings Vol. **27**, p. 459), thus exactly according to certain planes, and with a lens of 3 m focal distance, consequently with the object placed at 6 m from the lens, in which way figures were obtained approaching geometrical projections.

The two röntgenograms, one of the upper end, the other of the lower end of the femur were taken by the kind help of the late distinguished röntgenologist, Professor J. K. A. WERTHEIM SALOMONSON.

EXPLANATION OF THE PLATES.

PLATE I.

Fig. 1. — (Left) Femur of Pithecanthropus erectus, front view. Plane of figure the tangent plane of the most prominent back parts of the bone.

Of points not mentioned in "The Principal characters of the Femur", the figure shows, in the upper two third part of the shaft, a certain roughness caused by adherent small pyritoid concretions, moreover, as consequences of the excavating work, some superficial loss of small flakes and a somewhat larger one at the inner side of the lower end (about 9 cm from below). Of the anterior extremity of the condylus medialis a small fragment of bone got lost, exposing the spongiosa; this part appears smooth in the figure, as a consequence of the preparation for making the plaster cast. Conspicuous is on the epicondylus lateralis a flat eminence for insertion of the lower part of the intermuscular septum behind the vastus lateralis and crureus.

Fig. 2. — (Left) femur of Pithecanthropus erectus, inner view. At right-angles to Fig. 1. Particulars mostly mentioned in "The Principal Characters of the Femur". The rounded

form of the shaft (complete absence of an angulus medialis) is especially noteworthy. The lower arterial foramen (in upward direction) at 19 cm above the edge of the condylus medialis. This edge is incomplete anteriorly through the loss of the mentioned fragment.

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[1]) "Figures of the Calvarium and Endocranial Cast, a Fragment of the Mandible and three Teeth of Pithecanthropus Erectus", Proceedings Vol. 27, p. 459—464. (Plates I—XI).

Fig. 3. — (Left) femur of Pithecanthropus erectus, outer view. At right-angles to Fig. 1.

The peculiar arching of the shaft from above downwards in both figures, 2 and 3, clearly recognizable. Also the flattening of the posterior surface above the middle of the shaft. In this aspect also the trochanter major appears with a form different from the human trochanter. The strong eminence for the insertion of the lower end of the lateral intermuscular septum is a prominent feature in the distal extremity of the bone. The apparent roughness of the shaft in its upper two thirds is still more conspicuous than in Fig. 1.

PLATE II.

Fig. 4. — (Left) femur of Pithecanthropus erectus, from behind. Plane of figure the tangent plane of the most prominent back parts of the bone.

The great exostosis is seen in its full extension, clearly also the well marked linea aspera and the strong external supracondylar line, the total absence of a real internal supracondylar line. At the inner side of the former, clearly separated, the median buttress of the planum popliteum.

Fig. 5. — (Left) femur of Pithecanthropus erectus. View from above. The condyli below tangent to the plane of figure.

Shows the „angle of torsion" and the transversal inclination.

Fig. 6. — (Left) femur of Pithecanthropus erectus. View from below. The condyli from above tangent to the plane of figure.

Shows the shape of the articular surface in that aspect, the prominence of the lateral lip of the patellar surface, and the transversal inclination.

Fig. 7. — Right femur of a man, with similar exostosis. The exostosis was found by SCHWALBE in the anatomical theatre of Strassburg [1]). It seems that the man, a comedian who died at 50 years of age, never knew that his leg was abnormal. The dissection proved entirely sound surroundings of the exostosis and normal muscles. It appears that it does not in the least affect the normal forms of the other parts of the bone. The exostosis is certainly of the same character as that of the Pithecanthropus femur, also as regards place and extension. Only in the Pithecanthropus femur its upper part is much heavier and in the Strassburg-femur the lower portion more extended. Certainly SCHWALBE was right in remarking that the upper part of the Strassburg-exostosis belongs to the extensive connective tissue between the vastus medialis and the adductor muscles.

PLATE III.

Fig. 8. — Röntgenogram of the upper end of the (left) femur of Pithecanthropus erectus, from behind.

Although darkened in a large degree by the filling of many of the bone cavities with calcite and pyrite, the general character of the trajectoria is clearly recognizable. This is human. The static trajectorium of the erect attitude of WALKHOFF, ascending in oblique direction from the compact wall at the internal angle between the shaft and the neck and penetrating the head of the femur to arrive at the articular surface, is unmistakably present. Also the great arching trajectorium, the "Zug"trajectorium of WOLFF, which, starting from the trochanter side and arching upwards and inwards to the inferior part of the articular surface of the head, crosses the former trajectorium at right-angles. WALKHOFF attributes it to the working of the pelvis-fixing muscles. Moreover the meshes are narrow and the lamellae longitudinal as in Man; no large, rounded meshes as in the Anthropoid Apes.

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[1]) See note in "the Principal Characters of the Femur of Pithecanthropus Erectus", p. 734.

PLATE I

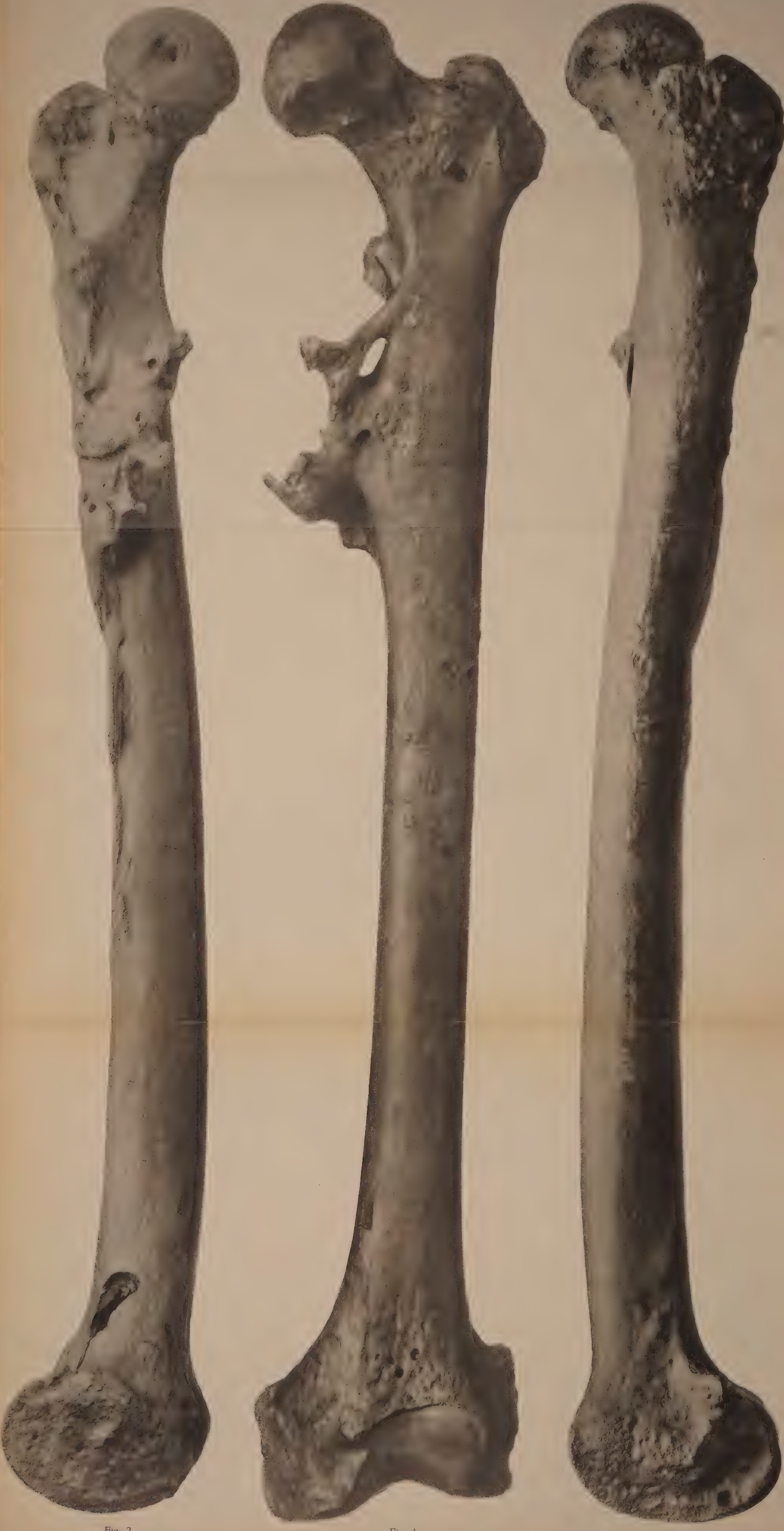

Fig. 2

Fig. 1

Fig. 3

EUG. DUBOIS: "FIGURES OF THE FEMUR OF PITHECANTHROPUS ERECTUS"

Heliotypie v. Leer & Co. Amsterdam

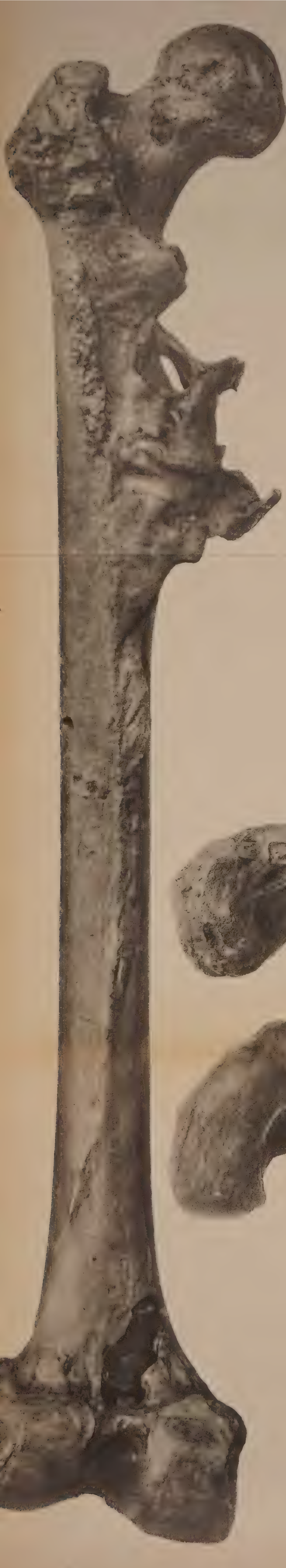

Fig. 4

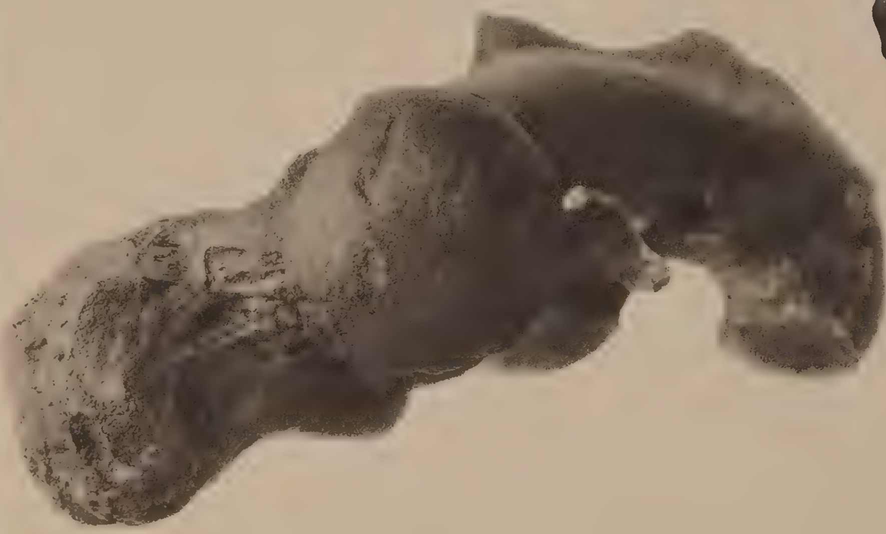

Fig. 5

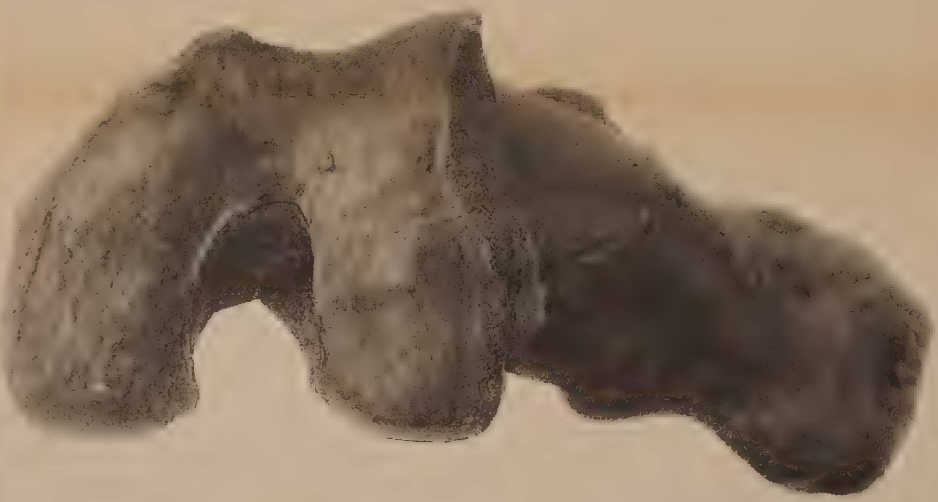

Fig. 6

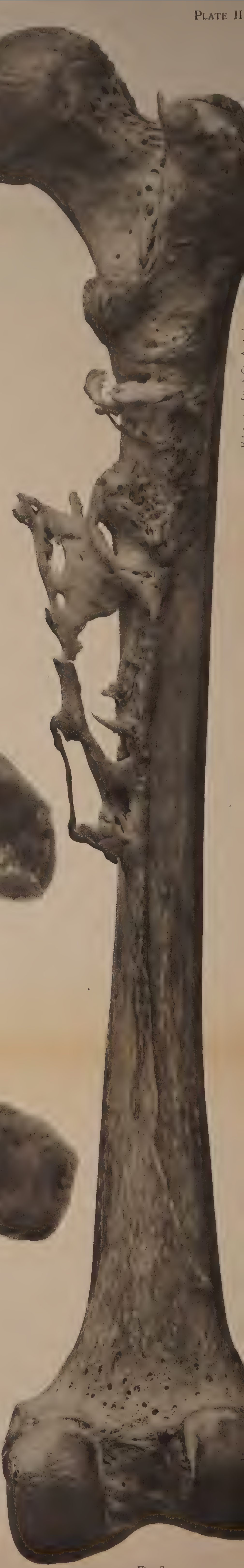

Fig. 7

EUG. DUBOIS: "FIGURES OF THE FEMUR OF PITHECANTHROPUS ERECTUS"

Proceedings Royal Acad. Amsterdam. Vol. XXIX.

EUG. DUBOIS: "FIGURES OF THE FEMUR OF PITHECANTHROPUS ERECTUS"

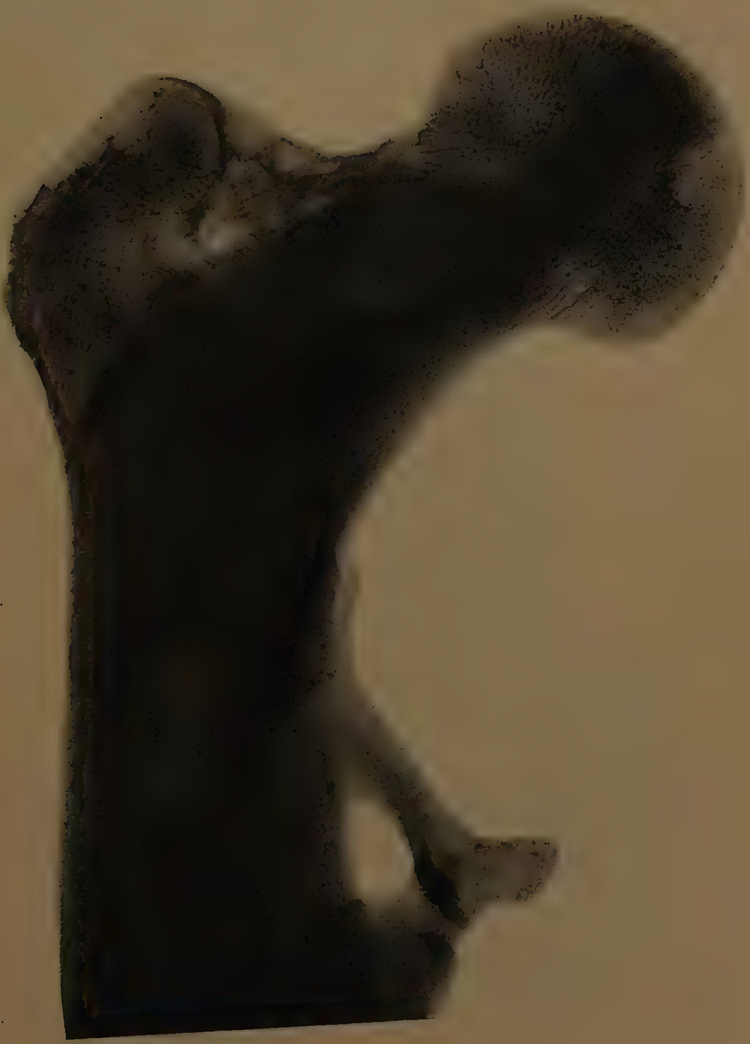

Fig. 8

Heliotypie v. Leer & Co., Amsterdam

EUG. DUBOIS: "FIGURES OF THE FEMUR OF PITHECANTHROPUS ERECTUS"

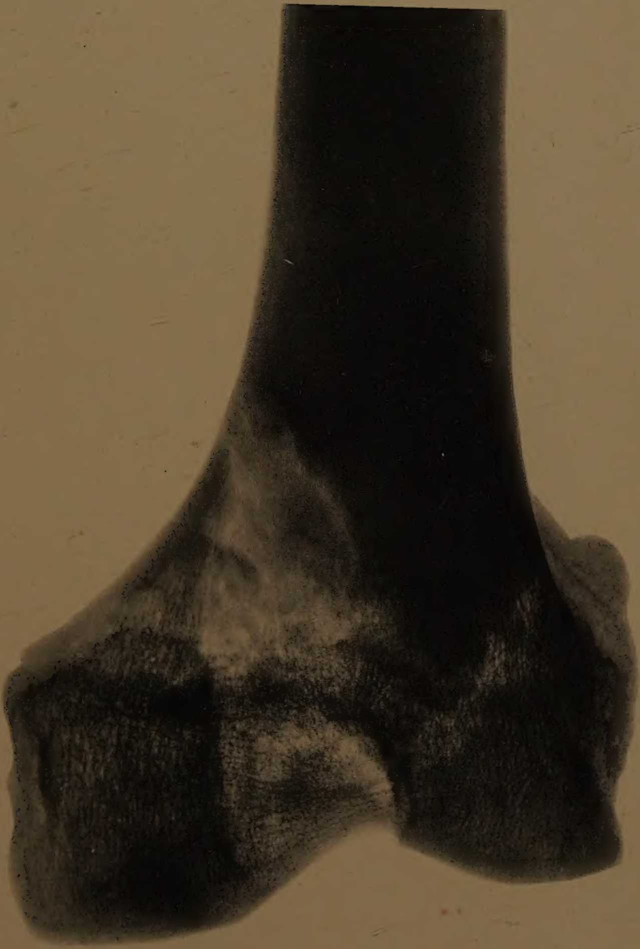

Fig. 9

Heliotypie v. Leer & Co., Amsterdam

PLATE IV.

Fig. 9. — Röntgenogram of the lower end of the (left) femur of Pithecanthropus erectus, from before.

Shows the narrow-meshedness, the vertical rectalinear lamellae ascending from the medial and the lateral condylus, and the lying down time-glassform inferior and transversal superior trajectoria of Man.

Certainly the femur of Pithecanthropus erectus, if not entirely constructed for the same locomotion as that of Man, was adapted for an erect gait and probably only a deviating locomotion for which the femur of Man is also fit, although not without artificial aid to the rest of his frame.